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POLYMORPHISM AT HIGH PRESSURES.

BY P. W. BRIDGMAN.

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POLYMORPHISM AT HIGH PRESSURES.

By P. W. Bridgman.

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Introduction.

In a number of preceding papers [1] the phase diagrams and the other thermodynamic data have been given for a number of polymorphic transitions under high pressures. In this paper complete data are given for ten new transitions, and incomplete data for five or six others. This brings the total number of polymorphic substances

1 P. W. Bridgman, (A) Proc. Amer. Acad., **47**, 439–558 (1912).
(B) Jour. Amer. Chem. Soc., **36**, 1344–1366 (1914).
(C) Phys. Rev., **3**, 126–141 and 153–203 (1914).
(D) Phys. Rev., **6**, 1–33 and 94–112 (1915).
(E) Proc. Amer. Acad., **51**, 53–124 (1915).
(F) Proc. Nat. Acad., **1**, 513–516 (1915).
(G) Proc. Amer. Acad., **49**, 4–114 (1913).
(H) Proc. Amer. Acad., **51**, 579–625 (1916).
(I) Proc. Amer. Acad., 52, 57–88 (1916).
Throughout the rest of this paper reference to these papers will be made by letter.

investigated to date to 37, including 34 new phases whose existence was not known before. In addition to substances which do show polymorphism, 94 other substances have been examined to 12000 kgm. at 20° and 200° without result. These substances are enumerated here.

This paper brings to a close, at least for the present, this series of investigations. The reason for this is not at all that all polymorphic substances have been studied, or that all interesting cases have been exhausted. The field is merely opened by these results. The reason is a practical one. Most of the substances that now suggest themselves for examination are not common chemicals that can be supplied by the large chemical houses, but require special preparation, for which I have not the facilities.

The number of substances investigated is nevertheless probably large enough to justify our pausing a little for examination of the entire field. The purpose of this paper, beyond the presentation of new data, is to coördinate somewhat this mass of results. To this end all the substances examined have been collected into various groups, chemical or not, according to the various clues which suggested an examination of them, and part of the discussion is concerned with these possible clues. The discussion also takes up a number of other general considerations connected with polymorphism, and tries to picture what may be the mechanism of a polymorphic change. It must be emphasized, however, that we cannot hope to get a complete explanation or description of polymorphism from data such as these. Data of many other kinds, particularly crystallographic data, are needed before the picture is complete.

New Data for Individual Substances.

Acetic Acid.— Several attempts were made before this substance could be obtained commercially in sufficient purity to show a good freezing point. The sample finally used was from the J. T. Baker Chemical Co., and by analysis was better than 99.9% pure. It is necessary to keep the acid as much as possible from contact with the air, because it rapidly absorbs moisture; to this end the glass stoppered bottle was kept sealed with paraffine.

The acetic acid was placed in the nickel steel cup, inverted under mercury. After prolonged contact with the steel at high temperatures and pressures there seems to be some slight chemical action; the

corners of the melting curve show somewhat more rounding, which in any event is slight, and on taking the apparatus apart a few bubbles of gas are set free. To avoid error from this effect measurements were begun about twice as far above the melting pressure as usual, and the cylinder was kept in cold water over night between runs. At the highest point attempted, 12000 kgm. and 165°, the reaction becomes so much more rapid that it did not seem worth while to make measurements. Runs were made with three fillings of the apparatus, two at high pressures and one near atmospheric pressure.

The equilibrium values of pressure and temperature are shown in

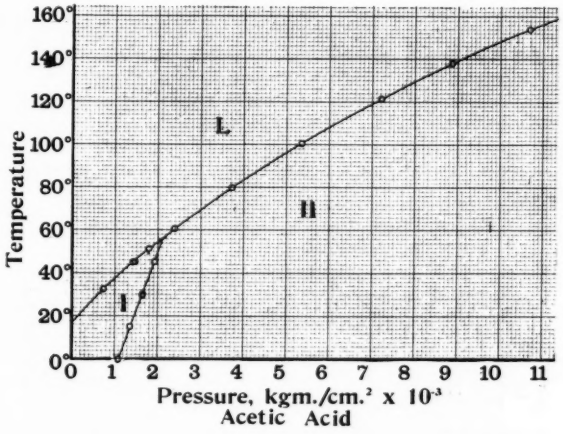

FIGURE 1. Acetic Acid. The observed equilibrium pressures and temperatures.

Figure 1, the observed changes of volume in Figure 2, the latent heat and change of internal energy in Figure 3, and the numerical results are collected in Table I. There is a second solid phase; the existence of this phase was first discovered by Tammann. No peculiarities are presented by the phase diagrams. It is to be noticed that the direction of curvature of the Δv curves on both melting lines is the normal one for solid-liquid.

There are a number of measurements of the thermodynamic data at atmospheric pressure. For the melting temperature there is 17.5°

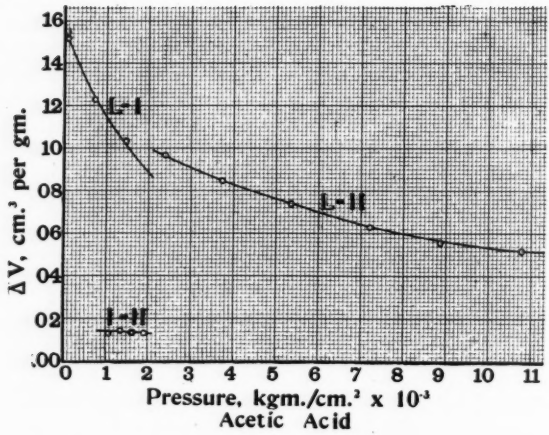

FIGURE 2. Acetic Acid. The observed changes of volume.

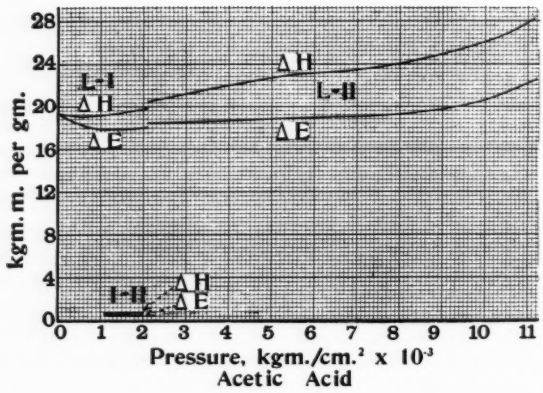

FIGURE 3. Acetic Acid. The calculated latent heats and the changes of internal energy.

TABLE I.

ACETIC ACID.

Pressure	Temperature	ΔV cm³/gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		LIQUID — I.			
1	16°.68	.1560	.02351	19.23	19.23
500	27 .8	.1330	2101	19.01	18.34
1000	37 .7	.1148	1869	19.09	17.94
1500	46 .5	.1006	1658	19.38	17.87
2000	54 .3	.0887	1470	19.75	17.98
		LIQUID — II.			
2000	54°.1	.1003	.01600	20.51	18.50
3000	69 .4	.0908	1463	21.27	18.55
4000	83 .4	828	1343	21.98	18.67
5000	96 .3	761	1240	22.68	18.88
6000	108 .2	700	1151	23.18	18.98
7000	119 .3	644	1072	23.57	19.06
8000	129 .6	598	1000	24.08	19.30
9000	139 .3	561	931	24.85	19.80
10000	148 .3	534	864	26.04	20.70
11000	156 .6	520	800	27.94	22.22
		I–II			
1074	0	.0140		.70	.55
1534	25	136	.0544	.74	.54
1994	50	131		.78	.52
		TRIPLE POINT, I–II — LIQUID.			
2100	55°.7	L–II .0992 L–I .0862 I–II .0130	.01585 .01432 .0544	20.58 19.79 .79	18.50 17.98 .52

by Sonstadt,[2] 16.55° by Pettersson,[3] 16.75° by Rudorff,[4] 16.75 to 17.00° by Raoult,[5] 16.59° by de Visser,[6] 15.62° by Abegg,[7] 16.54° by Meyer,[8] and 16.68° by Faucon.[9] In Table I, I have adopted the value given without reference in the recent edition of Stelzner, which is the same as the value of Faucon. For the latent heat there is 43.66 cal. between 2.9° and 5.6° by Pettersson,[3] 46.4 at the melting point by Marignac,[10] 46.3 by de Visser,[6] and 45.8 by Meyer.[8] The value of Table I, computed from Δv and $\frac{d\tau}{dp}$ is 45.1 cal. For the change of volume on melting Pettersson [3] gives 0.1252 cm.^{3} per gm., de Visser [6] 0.1595, Meyer [8] 0.1578, and Block [11] 0.1278. I find by extrapolation from 78 kgm. 0.1560. The specific heat of the solid is given by Guillot [12] as 0.627 at 4.5°, and that of the liquid at 16.5° as 0.473 by Massol and Guillot.[13] Schiff [14] gives for the liquid the formula $0.444 + 0.0_3709\ (t + t_1)$. There can be no doubt but that the value for the solid is erroneous.

The effect of pressure on the melting point has been measured by de Visser [6] up to 30 kgm.; he gives for the initial slope 0.02355 degrees per kgm. Meyer [8] calculates from his data 0.0233 for the initial slope, and I find above 0.02351. Tammann [15] finds a considerably lower value, 0.0220. The only measurements to higher pressures are by Tammann, who also gives the only previous data on the transition line between the two solids. His coördinates of the transition line differ widely from mine. At 0° his equilibrium pressure is 1145 kgm. against 1074 of mine, and at 50° it is 2170 against 1994. The difference cannot be explained by the width of the band of indifference. Tammann's melting curves both lie appreciably below mine; his triple point differs by 230 kgm. and 1.8° from mine. Tammann does not give the changes of volume.

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2 Sonstadt, Jahrber. Fort. Chem. 1878, **34**, and Chem. News, **37**, 199 (1878).
3 O. Pettersson, Jour. prak. Chem. (2), **24**, 296.
4 Rudorff, Ber. D. Chem. Ges., **3**, 390.
5 Raoult, Ann. Chim. Phys. (6) **2**, 66, 71 and 75.
6 de Visser, Rec. Trav. Pays Bas, **12**, 101 (1893).
7 Abegg, ZS. phys. Chem., **15**, 213 (1894).
8 J. Meyer, ZS. phys. Chem., **72**, 225 (1910).
9 Faucon, quoted in the Tables of the French Physical Society under date of 1910.
10 Marignac, quoted by J. Meyer, reference (8) above.
11 H. Block, ZS. phys. Chem., **78**, 385 (1911–12).
12 Guillot, Paris, J. B. Baillière et fils (1895). Thesis (?).
13 Massol and Guillot, C. R., **121**, 108 (1895).
14 Schiff, Lieb. Ann., **234**, p. 322.
15 G. Tammann, Kristallisieren und Schmelzen, p. 275.

The difference of compressibility, thermal expansion, and specific heats between the several phases may be found in the usual way.[16] Direct experimental values were found for the difference of thermal expansion of the liquid and I at 78 kgm., and for the difference of compressibility of II and I. For the difference of expansion ($\Delta\beta$) I found 0.00050, which is in rather good agreement with the value of Block,[11] 0.00048. It is somewhat of a puzzle that Block seems to be able to get good values for $\Delta\beta$, whereas his values for Δv are often widely in error. Using the experimental value of $\Delta\beta$ and the values for $\frac{d\Delta v}{dp}$ and $\frac{d\Delta H}{dp}$ that may be computed from the table, we find $\Delta\alpha = 0.0_464$ and $\Delta C_p = -0.016$ cal. The negative value for ΔC_p is improbable in spite of the experimental statement of this by Guillot.[12] If we assume that $\Delta C_p = 0$, the approximation usually made, the value of $\Delta\alpha$ becomes 0.0_465 and the value of $\Delta\beta$ 0.0_556. This shows again the insensitiveness of $\Delta\alpha$ to the value of ΔC_p. The fact that $\Delta\beta$ calculated with this assumption differs no more from the experimental value makes it probable that ΔC_p is really very small at atmospheric pressure.

The values of $\Delta\alpha$ and $\Delta\beta$ calculated at other points on the L–I and the L–II curves are shown in Table II, making the usual assumption that $\Delta C_p = 0$. This is probably a bad assumption on the L–I curve at 2000 kgm., because the value for $\Delta\beta$ becomes too small, and also because $\Delta\alpha$ does not check with the values for L–II and I–II. Also error is probably introduced by a too rapid increase of ΔH on the upper end of the L–II curve. If the calculations are carried through at 10000, $\Delta\beta$ is negative. On the I–II curve the experimental data showed that the difference of compressibility of I and II is not more than 0.0_51. This gives us a maximum value of $\Delta\beta$ 0.0_52. As mentioned above, the values given for $\Delta\alpha$ (L–I and L–II) do not check at 2000 with $\Delta\alpha$ (I–II); probably $\Delta\alpha$ (L–I) is too large.

In an unsuccessful search for other modifications pressure was carried to 12500 kgm. at 30° and 170°. It should be remembered that Tammann found some evidence for another form below 0°; I did not investigate this.

ACETAMIDE.— This substance has a second modification of the solid, not known before, the transition point being at 6000 kgm. at room temperature, and the transition line running nearly vertically. The material was obtained from Eimer and Amend. Two series of

[16] D, p. 100.

runs were made, separated by an interval of seven months. The first series of runs gave four points on the transition curve. The acetamide was used without purification for this run; it was placed in the inverted nickel steel cup under mercury. There was a rather large amount of impurity as shown by the moist appearance of the original material, and the very large amount of rounding of the corners of the melting curve. This rounding was so large that it was not possible to make accurate measurements on the upper end of the transition line, near the triple point, and much less to make even rough determinations of the melting data. This did not at that time seem a very

TABLE II.

ACETIC ACID.

Pressure	$\Delta\alpha$	$\Delta\beta$
	L–I	
1	$.0_464$	$.0_350$
1000	37	26
2000	20	15
	L–II	
2000	$.0_411$	$.0_46$
4000	$.0_577$	$.0_44$
6000	59	$.0_59$
8000	42	$.0_52$

serious matter, however, since the primary interest of this work was not in measuring more melting curves, and since the transition itself was sharp, showing that the impurity did not form mixed crystals. On working up the data it appeared, however, that there were some very slight indications that there were really three modifications instead of two. If there were three modifications, the volume of one of them must have been so close to one of the others that it was desirable to use as pure material as possible. A second series of runs was accordingly made with material which had been twice crystallized in the thermostat at constant temperature. Large perfe ctly trans

parent crystals were obtained, $\frac{1}{4}$ to $\frac{3}{8}$ of an inch in diameter, showing very well the hexagonal primitive form and the characteristic faces on the ends. The purity was still not perfect as shown by a slight remaining rounding of the melting curves, but it was nevertheless possible to make satisfactory measurements of the melting.

The observed equilibrium pressures and temperatures are shown in Figure 4, the observed differences of volume in Figure 5, the calculated latent heats and changes of internal energy in Figure 6, and the numerical values are collected in Table III. I did not think it worth while to try for a point on the melting curve nearer 12000 kgm., as rather

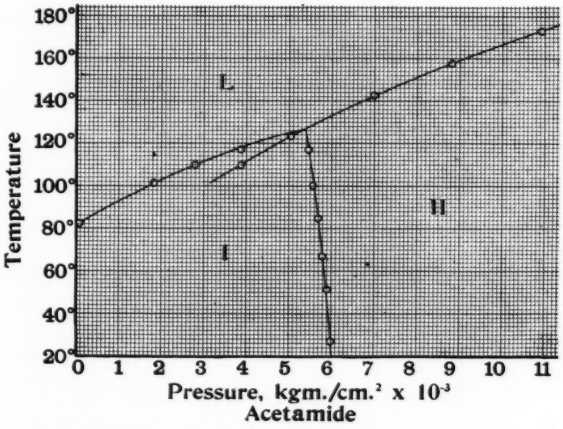

FIGURE 4. Acetamide. The observed equilibrium pressures and temperatures.

inconvenient manipulation would have been necessary to obtain it, and even then satisfactory measurements of Δv would not have been possible without taking the apparatus further beyond 12000 kgm. than I cared to. Furthermore, such a point was not necessary to establish the non-existence of other solid forms, because at 173° I found no new solid form up to beyond 12000. The inconvenience of manipulation referred to is caused by the very great subcooling that the liquid will support; after determining the point at 157.5° and 8800 kgm. it was necessary to lower the temperature 20° and raise the pressure to 12700 kgm. before the liquid could be forced to freeze. This means a superpressure of 6200 kgm. or a subcooling of 45°.

With the use of the purer sample the minute irregularities in the transition, which had given rise to the suspicion that there might be another modification, disappeared, but still other very minute consistent irregularities remained which leave me uneasily suspicious that

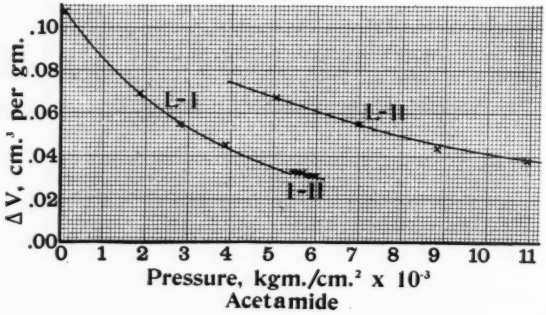

FIGURE 5. Acetamide. The observed changes of volume.

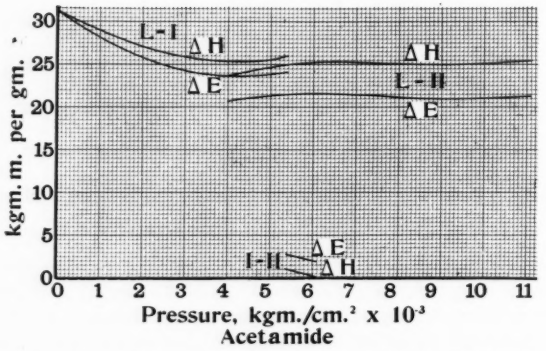

FIGURE 6. Acetamide. The calculated latent heats and the changes of internal energy.

somewhere below 75° the transition line may perhaps split into two inclined at a very slight angle. It would be very difficult to verify this suspicion, however, because of the increasing sluggishness of the

TABLE III.

Acetamide.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		Liquid — I			
1	81°.5	.1098	.01245	31.3	31.3
1000	93 .1	.0852	1076	29.0	28.1
2000	103 .1	.0668	0929	27.1	25.7
3000	111 .7	.0533	0792	25.9	24.3
4000	119 .0	.0429	0662	25.4	23.7
5000	125 .0	.0346	0538	25.6	23.9
		Liquid — II			
4000	111°.5	.0746	.01209	23.7	20.8
5000	122 .9	676	1083	24.7	21.3
6000	133 .1	609	0979	25.3	21.6
7000	142 .5	546	0897	25.3	21.5
8000	151 .1	492	0831	25.1	21.2
9000	159 .1	448	0774	25.0	21.0
10000	166 .55	412	0720	25.2	21.0
11000	173 .5	383	0672	25.5	21.2
		I–II			
6000	20°.0	.0302	−.357	.25	2.06
5930	40 .0	305	.241	.40	2.21
5835	60 .0	309	.190	.54	2.35
5720	80 .0	315	.161	.69	2.49
5590	100 .0	321	.144	.83	2.63
5440	120 .0	328	.132	.98	2.76
		Triple Point, Liquid — I–II			
5390	127°.0	L–I .0319	.00491	26.0	24.3
		L–II .0649	.01040	25.0	21.5
		I–II .0330	−.128	1.03	2.81

transition at low temperatures. I made an attempt at 0°, where the separation of the lines would be greater than at higher temperatures, but the transition is so very sluggish that II would not change into I even when carried 3000 kgm. into the region of I. Under the conditions it was useless to try to establish the existence of a transition with an abnormally small volume change and equilibrium pressure very close to that already measured, and I abandoned the attempt.

Acetamide is a substance of unusual interest because at atmospheric pressure it forms, in addition to the ordinary stable form of the solid, an unstable modification of such persistence that Körber [17] has been able to measure its melting curve up to 3000 kgm. Körber, in fact, says that the unstable form was always the one that crystallized out of the subcooled melt, and that inconvenient manipulation was necessary to force the stable form to appear. I was very anxious to measure the melting curve of the unstable form, because the general relations between melting curves of stable and unstable forms is still undetermined, in spite of work of Wahl [18] and Körber. Not once, however, did this unstable from appear in my apparatus, although several times the liquid was forced to freeze by raising pressure across the melting line at constant temperature. Once I thought that I had the unstable form, and measured the melting data for it, but it turned out afterward that this was merely a point on the melting curve of II prolonged into the region of I. That the new modification II is identical with the previously known unstable form is made impossible by the direction of its melting curve, and the volume relations. II is more dense than I, while the unstable form is less dense, and the melting point of the unstable form is about 10° below that of I, while the melting point of II, if it could be realized at atmospheric pressure, would be at least 30° below that of I. It may be that the failure of the unstable form to appear is connected in some way with the material of the container. For this experiment the acetamide was placed in a nickel steel container, whereas Körber used glass. It will be recalled that an analogous effect of the container was found in the case of ice [19]; the unstable ice VI crystallized out of the melt in the usual metal container, and the stable V could be forced to appear only by bringing glass somewhere into contact with the liquid.

The fact that the line L–II can be carried so far into the region of I is of interest. Ordinarily, when measuring points on the transition

17 F. Körber, ZS. phys. Chem., **82**, 45–55 (1913).
18 W. Wahl, Trans. Roy. Soc., **212**, 117 (1912).
19 A, p. 502.

curve I–II, working from lower to higher temperatures, II can be carried only an inappreciable distance into the region of I at temperatures above 100°. That is, if I has been recently present in the apparatus, so that II carries in its crystalline structure a nuclear memory of the structure of I, then II will change to I as soon as pressure is manipulated so that I is the absolutely stable form. But if I has been melted, and the liquid forced to crystallize to II, the sojourn in the liquid state now effaces all memory of I, and II will show very little tendency to change to I on being carried into its region of stability, but will melt to the liquid instead, if the temperature is not too far below the triple point. If, however, temperature is too far below the triple point (at 101.5° in an actual case), II will spontaneously change to I before the melting curve can be reached.

It was fortunate that I could obtain a very satisfactory measurement of the change of volume when II changed to I at 101.5° at a point 1800 kgm. distant from the transition line. This evidently

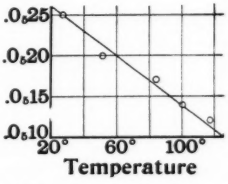

FIGURE 7. Acetamide. The observed differences of compressibility between the two solid phases.

gives, by a method independent of that usually used, the difference of compressibility between I and II. It turns out that II, the phase with the smaller volume, is on the average 0.0_512 cm.^{3}/gm. per kgm. more compressible than I between 3800 and 5600 kgm. The difference of compressibility between I and II along the transition line was also determined in the usual way from the difference of slopes of the isothermals above and below the transition point. This method shows that II is more compressible than I over the entire length of the transition line, the difference being pronouncedly greater at the lower temperatures. The observed values for $\Delta\alpha$, which show a gratifying regularity, are reproduced in Figure 7. At 101.5° the agreement by the two independent methods, 0.0_512 against 0.0_514, is unexpectedly good. The small difference may quite possibly be due to the difference of pressure range.

From the difference of compressibility between I and II the difference of thermal expansions and the difference of specific heats may be calculated in the usual way. The results are collected in Table IV. I is throughout more expansible than II, and has a smaller specific heat.

The difference of compressibility between liquid and solid may be approximately calculated in the usual way, on the hypothesis that $\Delta C_p = 0$. The results are shown in Table V. The behavior of $\Delta\alpha$ for L–II is remarkable, at first increasing with rising pressure and then falling. The effect probably really exists, and is not to be

TABLE IV.

ACETAMIDE.

Difference of thermal expansion and specific heat between I and II.

Temperature	$\Delta\beta$	ΔC_p gm.cal./gm.
20°	$+.0_420$	$-.013$
40	29	15
60	34	15
80	39	15
100	42	13
120	43	12

explained by experimental error, because the figures indicate that at the triple point I is less compressible than II, a result already reached by independent method. This is not the first time that we have found that a new phase in the neighborhood of the triple point is abnormally compressible.

The directly measured difference of expansion between L and I at approximately atmospheric pressure was 0.0_354. The value found by Block [11] was 0.0_342. The assumption that $\Delta C_p = 0$ probably does not give values of $\Delta\beta$ at higher pressures worth recording, because on this assumption we find that at atmospheric pressure $\Delta\beta$ has a

value much too large, 0.001 against 0.0005. This indicates that at least the initial values of $\Delta\alpha$ are a little too high.

A number of measurements have been made on acetamide at atmospheric pressure by other observers. For the melting point of the stable variety there is 82° to 83° by Hofmann,[20] 81.5° by Block,[11] and 80.1° by Körber.[17] The value for the specimen used above was 81.5°. The change of volume has been found to be 0.1507 cm.^{3}/gm. at atmospheric pressure by Block,[11] which is in inexplicable disagreement with

TABLE V.

ACETAMIDE.

Difference of Compressibility between the Liquid and the Two Solids.

Pressure	$\Delta\alpha$ L-I	$\Delta\alpha$ L-II
1	$0_4$41	
1000	30	
2000	21	
3000	15	
4000	10	$0_5$54
5000	$0_8$83	67
6000		74
7000		72
8000		60
9000		47
10000		39
11000		33

the value found above. The effect of pressure on the melting point has been measured by Körber,[17] who used the comparatively inaccurate method of varying temperature at constant volume. His melting curve shows considerably more curvature than mine, starting at a temperature lower by 1°.4, it is 3°.8 higher at 1600 kgm., and 1°.1 higher at 3000. This must have been a result of his method; the lower initial melting point and much premature rounding of his curves shows that his specimen must have been the impurer of the two. It

20 Hofmann, Ber. D. Chem. Ges., **14**, 2729.

is this evident inaccuracy in the method which leaves me unconvinced as to the cogency of his proof that the melting curves of the stable and unstable forms are approximately parallel.

CARBAMIDE.— This was obtained from Eimer and Amend and was used directly without further purification. The purity was fairly high, as was shown by the melting point. At atmospheric pressure I found for my specimen 131.7°, which agrees within the limits of error of the previous work with the only published value that I have found, 132° by Liubarvin.[21] At least six different runs were made with this substance. For all except the least important it was hammered dry and cold into the requisite forms. It may be easily melted into the forms, but not without some slight decomposition, so that it seemed best to avoid this possibility. Under pressure decomposition takes place with increasing rapidity above 150° so that accurate measurements could not be made above this. The carbamide was placed in different sorts of containers for the different runs. At first it was hammered dry into the nickel steel shell and used with a mercury seal. But this resulted in rupture of the shell. The dissolving action of kerosene is slight, so that it was possible to make one run with the pressure transmitted directly to the carbamide by kerosene. This gave good values for the equilibrium values of pressure and temperature, but not consistent values for Δv, presumably partly because of a very slight dissolving action. In the final arrangement the carbamide was hammered into compact cylindrical forms and placed loosely in detached hunks beneath the surface of mercury, and prevented from rising to the surface by a clip of obvious design. Carbamide is quite unusual with regard to its distortion during a transition. The growth of one modification at the expense of another takes place in such a direction that a cylindrical block increases in diameter. This increase of thickness may develop considerable pressure, as shown by the bursting of the nickel steel shell. Even the blocks which were placed loose beneath the surface of mercury had, after several transitions, so swelled laterally as to tightly fill the shell, just as if they had been melted into position. This lateral growth, besides being very inconvenient because of the rupture that it may produce, may also produce very appreciable error in the measurements of Δv, because of internal strains. Because of this effect the measurements of Δv of the first runs were irregular and had to be discarded, and with the final arrangement, loose hunks under mercury, the apparatus had

21 Liubarvin, Ber. D. Chem. Ges., **3**, 305.

to be set up again after so many transitions had run as to jamb the carbamide tightly against the walls of the shell. At higher temperatures there is another source of error in measurements of Δv because of incipient decomposition.

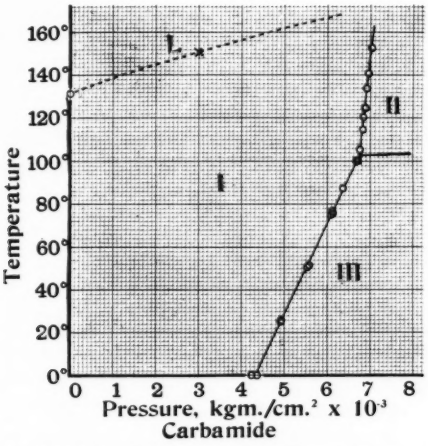

FIGURE 8. Carbamide. The observed equilibrium pressures and temperatures.

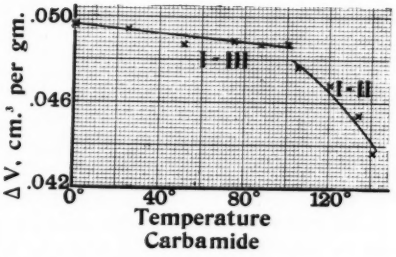

FIGURE 9. Carbamide. The observed differences of volume.

The equilibrium curves, with the observed pressure and temperature points, are shown in Figure 8, the values of Δv determined after the proper procedure had been discovered are shown in Figure 9, the

calculated values of latent heat and the change of internal energy in Figure 10, and the numerical values are collected in Table VI.

There are three modifications of the solid, but it was possible to make observations on only two of the transition lines because of the unusual volume relations. At lower temperatures there is only one transition line, I–III, but at 102.3° there is a triple point, and the line splits in such a way that almost all the change of volume remains with one of the lines, I–II, and almost all the heat of transition with the other. The change of volume between II and III is so small that it was not possible to measure points on this line, the motion of the piston accompanying this transition being only 0.001 of an inch. Apart from the evidence afforded by the sharp change of direction of I–III, the existence of the line II–III was verified by direct observa-

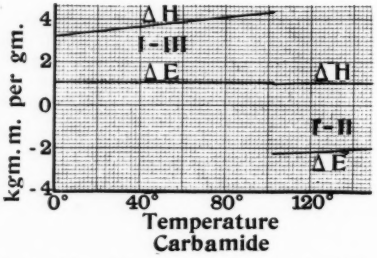

FIGURE 10. Carbamide. The calculated latent heats and the changes of internal energy.

tion, by varying temperature at constant volume and plotting the resulting change of pressure. A discontinuity in this curve of the appropriate order of magnitude was found, but of course this method does not give accurately the coördinates of the transition line.

Along with an abnormally small change of volume and a fairly high latent heat goes, of course, a very small slope for the line II–III. This slope was found by calculation from the data for the other lines at the triple point to be only 0.7° per 1000 kgm., by far the smallest slope yet found. It should be pointed out, however, that this calculated value was found from the difference of two very nearly equal quantities, so that it may be in error by a rather high percentage. The relation of the curves for the change of volume makes it perfectly certain, however, that the slope is positive.

There is the usual variation of the velocity of transition with temperature. At temperatures above 130° the transition is so rapid that no measurements of the rate were possible, whereas at 0° it was a matter of an hour or two for the pressure to approach within values

TABLE VI.

CARBAMIDE.

Pressure	Temperature	ΔV $cm^3/gm.$	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		I–III			
4320	0°.0	.04962	.04210	3.22	1.08
4795	20 .0	4942	"	3.44	1.07
5270	40 .0	4921	"	3.66	1.07
5745	60 .0	4901	"	3.88	1.06
6220	80 .0	4880	"	4.09	1.06
6695	100 .0	4860	"	4.31	1.05
		I–II			
6737	100°.0	.0482	.1803	.98	−2.25
6848	120 .0	465	"	1.01	−2.17
6959	140 .0	442	"	1.01	−2.06
7070	160 .0	413	"	.99	−1.93
		TRIPLE POINT			
6750	102°.3	I–III .04858 I–II .0480 II–III .0006	.04210 .1803 .00065	4.33 1.00 3.33	1.05 −2.24 3.29

differing by 700 kgm. from above and below. It was possible at 0°, however, by artificially changing the pressure and watching the subsequent reaction, to shut the pressure within limits only 60 kgm. apart.

The superpressure required to start the reaction also varies greatly; on one occasion 1750 kgm. beyond the equilibrium point was necessary at 0°.

Carbamide is an unusual organic compound with respect to its melting as well as with respect to its solid transitions. At 150°, in the search for other solid modifications, the melting data were approximately determined. The melting pressure is shown by a cross in Figure 8 and the approximate location of the melting curve is shown by the dotted line. The change of volume at 150° is very low for a melting, about 0.01 cm.^{3}/gm. This, together with the unusual flatness of the melting curve, a flatness that one associates with the melting of a metal rather than of an organic compound, aroused the suspicion that this point might really belong to a solid transition instead of to a melting. To test this, another run was made at 124°, slightly below the melting point at atmospheric pressure, and no transition of any kind found. It was for this run that the carbamide was melted into the form, as mentioned above. That the melting curve has approximately the location shown is also indicated by the fact that on one occasion, on trying to extend the I–II line to 170°, the transition entirely disappeared, doubtless because of melting. It has already been explained that the decomposition makes it useless to try for accurate coördinates of the melting curve.

The direct experimental measurement of the difference of the compressibility of the several phases did not give results accurate enough to justify an attempt to calculate $\Delta\beta$ and ΔC_p. It seems established, however, that I is less compressible than II, and that the difference is in the vicinity of the order of 0.0_54 cm.^{3}/gm. per kgm., which is fairly high. It is also probable that I is less compressible than III, but the difference between I and III is considerably less than the difference between I and II. The difference of compressibility between I and II, large as it is, is not nearly large enough to account for the rapid drop of Δv between I and II with rising temperature. It is very probable, therefore, that II is more expansible than I, and that the difference is of the order of 0.0001 cm.^{3}/gm. per degree.

Camphor.— This material was obtained from Eimer and Amend, "gum camphor, refined, powdered," and was used without further purification. It was hammered cold into the inverted cup, and pressure transmitted to it by mercury. The reason for trying this substance was that it is known to have an abnormally steep melting curve, the rise of temperature being about 130° for 1000 kgm.[22] This sug-

22 G. A. Hulett, ZS. phys. Chem., **28**, 629 (1899).

gested that it might be abnormal in other respects, and might possibly show other modifications. It does as a matter of fact have at least six modifications, the complication of its phase diagram being equalled or surpassed only by water and ammonium nitrate. It is unfortunate that it was not possible to make measurements with as great accuracy as was possible for many other substances. In fact the uncertainty in many of the measurements of the change of volume is so great that I have not attempted to estimate from them the most probable value of the change of volume or to calculate the latent heats. There can be no question, however, that the existence of the transition curves in approximately the situations indicated has been established. It was a matter of some difficulty, involving considerable time, to be sure of as much as this. More than a month was spent in getting the data given below; to obtain accurate values of the changes of volume and the latent heats in addition would have taken many times longer, if indeed it would have been possible at all. In the present state of our knowledge of polymorphism it did not seem that all this effort on a single substance would have been worth while.

The phase diagram is shown in Figure 11, the curves for Δv in Figure 12, the latent heat and the change of internal energy in Figure 13, and the numerical values in Table VII. The melting curve indicated in Figure 11 is taken from the data of Hulett.[22]

It will give an idea of the various difficulties and assist in forming an estimate of the accuracy of the work to describe the curves somewhat in detail. On the III–IV curve the reaction is very slow and the limits of indifference wide. This does not affect the accuracy of the change of volume, for which fairly satisfactory values were obtained, but may affect the equilibrium values, and so the slope and the latent heat. The III–IV curve is, however, determined with considerably greater accuracy than any of the others. On the II–V and the IV–V curves it is difficult to measure either the equilibrium or the Δv values because of the very small change of volume and the slight separation of the curves. Let us suppose that we are trying to get a point on the IV–V curve, lowering pressure from above. The pressure steps have to be made very small, because of the small change of volume, and so the measurements consume much time. Furthermore, after the reaction has once started, one cannot release the pressure far enough to ensure the completion of the reaction without overstepping the II–V line, and so getting the reaction II–V mixed up in the effect; no amount of time will give a good value for Δv. It does no good to attempt to ensure the completion of the reaction in the narrow region

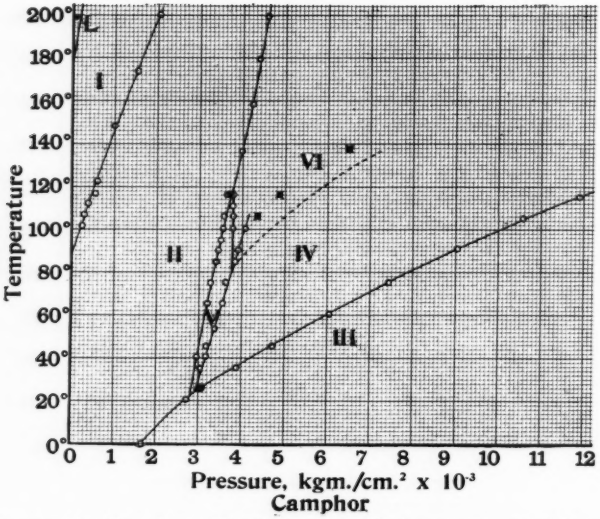

FIGURE 11. Camphor. The observed equilibrium pressures and temperatures. On the line IV–VI measurements could not be made on the reversible transition. The crosses show the points where metastable IV changes spontaneously to VI.

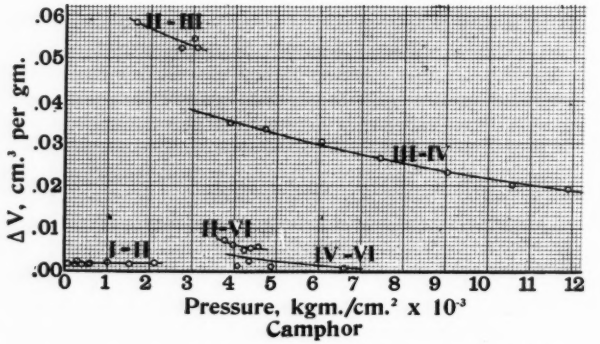

FIGURE 12. Camphor. The observed differences of volume.

between IV and II by raising or lowering the temperature, as is possible in the case of some other substances, because the boundaries of the region of existence of V are so nearly vertical that a change of temperature does not carry the pressure far enough away from the equilibrium

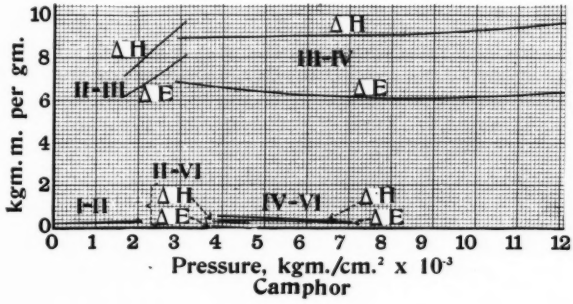

FIGURE 13. Camphor. The calculated latent heats and the changes of internal energy.

value to ensure completion of the transition. The total change of volume from IV to II can be determined with some accuracy, however, by taking pressure steps long enough to step over the region of V.

TABLE VII.

CAMPHOR.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			I–II		
0	87°.1	.00187	.0635	.106	.106
500	117 .6	"	.0589	.124	.115
1000	146 .2	"	.0555	.141	.122
1500	173 .2	"	.0528	.158	.130
2000	199 .1	"	.0510	.173	.136

Table VII, Continued.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			II–III		
1660	0°	.0585	.0223	7.2	6.2
2130	10	563	.0200	8.0	6.8
2660	20	540	.0178	8.9	7.5
			III–IV		
3000	25°.3	.0377	.01260	8.93	7.83
4000	37 .6	348	1204	8.96	7.57
5000	49 .4	320	1148	8.99	7.39
6000	60 .6	296	1092	9.03	7.26
7000	71 .2	273	1037	9.07	7.15
8000	81 .3	252	0982	9.12	7.10
9000	90 .8	234	0926	9.21	7.10
10000	99 .8	218	0870	9.32	7.14
11000	108 .2	202	0815	9.46	7.24
12000	116 .1	188	0760	9.62	7.36
			IV–V		
2880	20°				
3460	60		.0687		
3900	90				
			II–V		
2800	20°		.133		
2959	40		.119		
3137	60		.107		
3333	80		.098		
3548	100		.089		
3783	120		.082		

Table VII, Concluded.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			II–VI		
3782	120°	.0069	.084	.321	.060
4009	140	61	.093	.272	.028
4217	160	57	.101	.244	−.003
4407	180	54	.110	.222	−.016
4582	200	52	.119	.206	−.032
			VI–IV		
4000	87°.5	.0037	.025	.53	.39
5000	106 .0	24	.019	.47	.35
6000	121 .5	14	.014	.39	.31
7000	134 .0	06	.008	.29	.25
			V–VI		
3780	90°		∞	0	
3780	110				

In determining points on the V–VI line there is the same difficulty as on the IV–V line; the difficulty increases toward the triple point at the upper end.

On the VI–IV line the points could not be determined with any approach to accuracy because this is a reaction that will run in only one direction. If pressure is released, starting with IV, the reaction to VI will run with a discontinuous change of volume, but on increasing the pressure again within reasonable limits the transition cannot be made to run backwards. This does not mean at all that IV is an unstable form. The behavior here is much like that on the rising branch of the curve for mercuric iodide. The amount by which the phase VI may be carried into the region of IV without the transition running is very large. At 110°, the transition from VI to IV did not run when pressure was increased to 9000 kgm. The points on this

curve had to be obtained by lowering the temperature after every reading far enough to reach the region where the reaction to III runs. On increasing temperature again beyond the III–IV line, the reaction from III to IV was certain to run, so that one could be sure in this way of starting with IV. One consequence of the great lag of the reaction from IV to VI is that the changes of volume determined from these measurements are certain to be in error, unless the compressibility of the two phases should by accident happen to be the same, because these are not the differences of volume at the equilibrium point, but at some other point. The measured difference is presumably too large. The difficulty of measurement is further increased by the fact that the difference of volume is excessively small. The discontinuity in the piston displacement at the last point measured on this curve, at 137°, was only 0.0018 of an inch.

The transition from V to IV shows the same lag as that from VI to IV, although the lag is not so obstinate. If temperature is raised on the phase II to somewhere between 50° and 80°, the pressure being at about 2000 kgm., and then pressure increased at this temperature, the reaction from V to IV will not run, even if the pressure is increased several thousand kilograms beyond the transition value. It is impossible in this way to obtain points on the IV–V line, but only the II–V line will be found. This curious disappearance of the IV–V line was the cause of much mystification before the explanation was found. To be sure of getting points on the IV–V line, the phase IV should be produced by first increasing pressure at low temperature, so as to force the appearance of III, and then raising temperature across the III–IV line. If the phase IV has once been formed, and pressure is decreased so as to produce V, the transition may be made to run in the reverse direction by increasing pressure again. That is, the phase IV will be produced from V if IV has existed in the apparatus only a short time previous. Under such circumstances there seem to be some nuclei left about which the formation of IV can begin. A precisely similar behavior has been found for some of the varieties of ice.

The points on the II–VI line could be obtained with fair definiteness, and the values of Δv were also self consistent enough to warrant including them in Figure 12. The concave side of the equilibrium line II–VI is toward the temperature axis, which is the reverse of the case for II–V. There are indications that the curve II–VI may split again at its upper end, there being a modification VII; an appearance at 200° like that of two equilibrium points close together suggested this. The

points for Δv (II–VI) at 180° and 200° lie higher than the others would demand, and suggest the same possibility. Furthermore, the direction of curvature would be explained by the existence of a new modification. I was not able to settle the point, however, and have drawn only one curve in the diagram. This is the curve which best fits the equilibrium points. It is very probable, however, that at the triple point II–V–VI the curve II–VI should be steeper than drawn, and the curve II–V less steep. This is indicated by the latent heat relations.

On the II–III line only two points were determined, but the line has nevertheless been indicated in Table VII as having a curvature in the normal direction. The existence of curvature in this direction is demanded by the latent heat relations of II–III–IV–V at the approximately quadruple point, and the actual amount of curvature can be very approximately calculated from the data for the other curves. But to detect this curvature experimentally would have been difficult, because the breadth of the band of indifference is sufficient to conceal the effect on a curve so short.

On the I–II line a considerable element of uncertainty is introduced because the change of volume is so small that equilibrium points cannot be obtained, but the transition runs entirely to completion when it has once started. The transition is fairly rapid, however, and runs without much trespassing of the equilibrium pressure. The points shown in the diagram are the means of the pressures at which the transition ran spontaneously from above and below; these two pressures differed by from 50 to 100 kgm. The values of Δv cannot be determined with much percentage accuracy because of their smallness; it was not possible to tell from the data whether Δv increases or decreases with rising temperature, and in the computations Δv has been assumed to be constant. The points on the I–II line were not determined at the same time as the other points, but nearly one year later. The same specimen of camphor was used.

In view of the uncertainty of the Δv values on the II–V, IV–V, and V–VI curves, I have not attempted in Table VII to give even the most probable values for the change of volume or latent heat. The individual determinations of these changes of volume are chaotic; except for being of the same order of magnitude they offer no justification for the choice of any one set of values. I have, therefore, not included the experimental points in Figure 12. One is in a position to say this much, however; on the lower ends of the curves II–V and IV–V the two changes of volume should add up to the total change II–IV which is indicated in Figure 12, and which was determined with fair consis-

tency experimentally; with a little less confidence, but still with fair accuracy, one may say that near 120° the changes of volume II–V and V–VI must add to the experimental values given in the figure for II–VI; and with much less accuracy one may demand that at the triple point IV–V–VI the changes IV–V and V–VI check with the value given in the figure for IV–VI. It must be remembered that the change IV–VI could not be determined on the equilibrium line, and so in all probability is not accurate.

With regard to computing the latent heat, the difficulty of determining $\frac{d\tau}{dp}$ accurately is greatly exaggerated because some of the transition curves run so nearly vertical; a very small change in the angular direction of a curve produces an enormous percentage change in the value of $d\tau/dp$, and so in the latent heat. Under the circumstances the only means of getting Δv and ΔH is one of trial and error, demanding that the additive relations at the triple points shall hold. It did not seem to me that the accuracy of the rest of the work would justify such an attempt. In the figures and the table I have, therefore, given the values of Δv and ΔH for only five of the curves. In order of certainty these are: III–IV, II–III, II–VI, I–II, and VI–IV, the last being of a higher order of uncertainty than the others.

On the III–IV line satisfactory measurements were made of the velocity of transition and the width of the band of indifference. These results have been described in a previous paper.

On the III–IV curve also rough values of the difference of compressibility could be determined. III is more compressible than IV over the entire curve; at about 7000 kgm. the difference is of the order of 0.0_525 cm.^{3} per gm. per kgm., rising to perhaps twice this value at the lower end, and falling to not less than two thirds of it at the upper end. The uncertainty in these values, and also those of ΔH and Δv is so great that it did not seem worth while to try to get $\Delta\beta$ or ΔC_p. Because of incompleteness of the transition etc. it was not possible to get good values of $\Delta\alpha$ or any of the other curves.

In a recent paper Wallerant [23] has described camphor as having three modifications at atmospheric pressure. It crystallizes from the melt in the cubic system. On cooling, the cubic modification changes at 97° to a feebly doubly refracting rhombohedric form, which at −28° is transformed again to a strongly doubly refracting rhombohedric form. These transition points of Wallerant are both about 10°

23 F. Wallerant, C. R., **158**, 597 (1914).

higher than mine. A linear extrapolation of my points on the II–III line would indicate −36° as the transition temperature at atmospheric pressure, and the probable curvature of this line would bring it down to somewhat below −40°. The discrepancy may possibly be due to still another modification, with a triple point on the line II–III below 0°. My point corresponding to Wallerant's 97° is at 87°. The discrepancy cannot be due to impurity of my specimen, because there was no preliminary rounding whatever of the corners of the isotherms. There is, however, a possible uncertainty of two or three degrees in my value 87°, as may be judged from the irregularity of the points at the lower end. I do not consider that this uncertainty can be possibly large enough to account for the discrepancy.

Wallerant's paper did not become known to me until all the other transition lines of camphor except I–II had been investigated. If it had not been for his paper, this transition would have entirely escaped me, because as has been previously explained, only in rare cases have I made especial search at atmospheric pressure for new modifications, but have accepted absence of mention of such transitions as presumptive evidence that there are none. This example brings out that in exceptional cases, where the transition line is very steep, or the change of volume very small, my method of exploration may possibly leave new transitions undiscovered. Camphor is a particularly unfavorable case, because both the transition line is very steep, and the change of volume very small.

Potassium Acid Sulfate.— This was obtained from Eimer and Amend, of the "tested purity" grade. Two sets of runs were made; the one gave all the high pressure points, and the other, with the low pressure apparatus, gave two points at nearly atmospheric pressure. Immediately before use it was heated to 100° in vacuum for several hours to remove the moisture. For the high pressure runs it was hammered cold into an open steel shell, and pressure was transmitted directly to it by kerosene. For the low pressure run it was melted into a glass tube, the glass removed, and the specimen placed loose in the pressure chamber, in direct contact with the kerosene.

$KHSO_4$ has four modifications. The existence of forms other than the ordinary low temperature form does not seem to have been known before, although there are two transition points and three modifications at atmospheric pressure. I was fortunate not to miss altogether the other modifications. At room temperature no new form was found out to 12000 kgm., although a transition line was crossed at 7000 or 8000. The reason for this is that at 20° the reaction is very sluggish,

so that a superpressure of 5000 kgm. will not start it. At 200° a small transition was found at about 2000 kgm., so small that I had to repeat the work before I could be sure of it. If the transition had been at 1000 instead of 2000, it would have been so near the end of the stroke that it would have been missed altogether. This experience shows that by making runs out to 12000 at 20° and 200° one cannot be sure that there are no transitions in the region unless it is certain that there are no transitions at atmospheric pressure between 20° and 200°; it is not sufficient warrant for the absence of a transition at atmospheric pressure, even for a common chemical, that no one has noticed it and

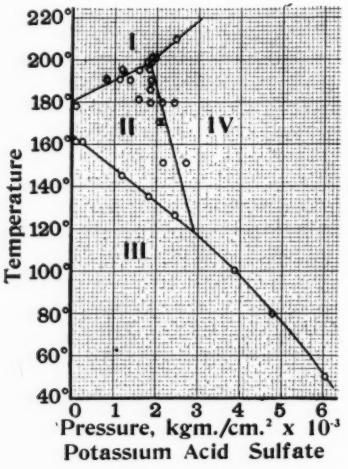

FIGURE 14. Potassium Acid Sulfate. The observed equilibrium pressures and temperatures.

tabulated it. It is possible, therefore, that some of the substances which I have examined for transitions without result may really have transitions, since I have always assumed that if a substance has not been tabulated as polymorphic it has no transition at atmospheric pressure. I have found one or two other examples of new phases at atmospheric pressure not known before.

The equilibrium values of pressure and temperature are shown in Figure 14, the values of Δv in Figure 15, the computed values of latent heat and change of internal energy in Figure 16, and the collected

numerical results in Table VIII. As is evident from the irregularity of the points, there are difficulties in the way of accurate measurement that need comment. On the II–IV line the change of volume is so small that it was not possible to obtain equilibrium values of the pressure even by the method of artificially varying pressure after the

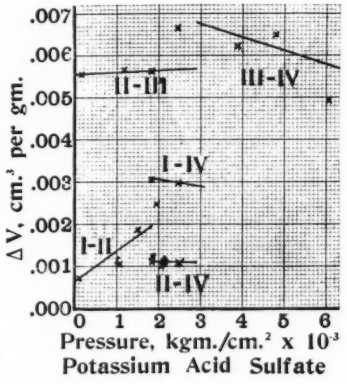

FIGURE 15. Potassium Acid Sulfate. The observed differences of volume.

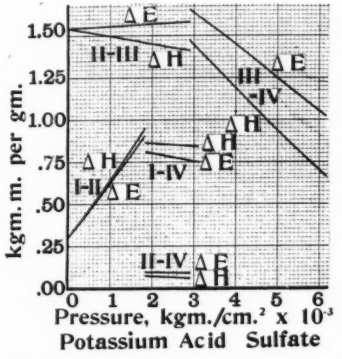

FIGURE 16. Potassium Acid Sulfate. The calculated latent heats and the changes of internal energy.

transition was partly completed. When the transition once started it ran rapidly to completion in less than fifteen minutes. The points shown in Figure 14 are the pressures of spontaneous starting of the transition, from IV to II with decreasing pressure, and from II to IV with increasing pressure. The true equilibrium line lies somewhere in the region limited by these points; there is no reason why it should lie in the center of the region. The actual position of the curve as shown was determined from the conditions of compatibility at the triple points. The curve I–II also has a small change of volume, but it was large enough so that the equilibrium values of pressure and temperature could be found when both phases were present simultaneously. On the line III–IV, which has the largest Δv of all, equilibrium points could be found in the regular way. The difficulty with this line is in the rapidly increasing slowness of the reaction toward the lower temperatures. At 50°, the equilibrium value could not be found to better than 750 kgm., even when both phases were present together, and it required more than one hour for the transition to run to apparent completion more than 2500 kgm. below the equilibrium pressure. This slowness doubtless has something to do with the bad Δv value at 50° on III–IV. It was quite out of the question to try for lower points on this line; it has been mentioned that at 20° the transition will not start at 12000, and at 50° it required a superpressure of 4000 kgm. to start the transition. The points on the II–III line presented little difficulty.

TABLE VIII.

POTASSIUM ACID SULFATE.

Pressure	Temperature	ΔV cm³./gm.	$\frac{dr}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			I–II		
1	180°.5	.00066	.0099	.302	.302
1000	190 .4	.00137	"	.642	.628
2000	200 .3	.00209	"	1.000	.958
			I–IV		
2000	201°.5	.00307	.0169	.862	.801
3000	218 .4	.00290	"	.843	.756

Table VIII, Continued.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			II–IV		
1810	200°.0	.00113	−.075	.071	.093
2075	180 .0	.00112	"	68	91
2340	160 .0	.00111	"	64	90
2610	140 .0	.00111	"	61	90
2875	120 .0	.00110	"	59	90
			II–III		
1	164°.2	.00556	−.0158	1.54	1.54
1000	148 .4	561	"	1.50	1.55
2000	132 .6	566	"	1.45	1.57
3000	116 .6	571	"	1.41	1.58
			III–IV		
3000	116°.4	.0068	−.0182	1.46	1.66
4000	97 .5	.0064	−.0199	1.19	1.45
5000	76 .1	.0061	−.0229	.93	1.24
6000	51 .4	.0058	−.0268	.70	1.05
			Triple Point, I–II–IV		
1830	198°.6	I–II .00197	.0099	.939	.903
		II–IV .00113	−.075	.711	.092
		I–IV .00310	.0169	.865	.809
			Triple Point, II–III–IV		
2900	118°.2	II–III .00570	−.0158	1.41	1.58
		II–IV .00110	−.075	.057	.089
		III–IV .00680	−.0181	1.47	1.66

Because of the smallness of the change and the width of the band of indifference on the lines I–II and II–IV, several of the early measurements of the change of volume were not good and had to be discarded. These comprised three points on II–IV, one on I–II, and one on I–IV. In virtue of the relations at the triple points one can be fairly certain of the values of Δv for these lines.

By a curious grouping of the discrepancies of the early measurements of I–II and II–IV, it looked as if possibly there were still another modification with excessively small volume change. Subsequent careful exploration failed to substantiate this surmise.

The order of determination of the points was as follows: first one on I–IV, then several on I–II and II–IV, then the points on III–IV, then II–III, II–IV, I–II, and I–IV again, and finally two points with the low pressure apparatus. The complete run at high pressures with the apparatus set up with one filling and pressure never entirely released extended over seven days; there was no decomposition or change in the $KHSO_4$ in this time as shown by the fact that the last determined I–IV points fall exactly in line with the first.

The point with the low pressure apparatus on II–III does not require especial comment. To obtain the Δv value of I–II special procedure was necessary because of the sluggishness of the transition. On passing over the line from II to I, the temperature was raised to 190°, and then lowered, in order to ensure completion of the transition. The sluggishness was so great that it was not possible to obtain an equilibrium point on I–II at low pressures. At 180° the transition from I to II could not be started by a pressure of 1000 kgm., the limit of the apparatus.

There are no previous data for the polymorphic transitions for comparison, the existence of the modifications not having been known before. The melting point of $KHSO_4$ at atmospheric pressure is given as 200° by Mitscherlich [24] and 210° by Schultz-Sellack.[25] I found it to be at any rate higher than 200°.

The accuracy of the measurements does not justify an attempt to compute the difference of compressibility of the four forms. It can be stated, however, that what difference of compressibility there is will be found to be very small. In this connection it should be noted that along the line I–II Δv increases with rising pressure, and that along III–IV it falls. Both these effects are unusual. The change along I–II points to a thermal expansion of I abnormally greater than

24 Mitscherlich, Pogg. Ann., **18**, 152 (1830).
25 Schultz-Sellack, Jahresber., 1871, 217.

that of II. The direct measurements with the low pressure apparatus showed that the expansion of I is of the order of 0.0005 cm.^{3} per gm. greater than that of II, and that of II 0.00004 greater than III. On the III–IV line, the indications are that III is considerably more expansible than IV.

It is of interest to notice that the triple point II–III–IV is the first case of its kind that has been found. All three transition lines meeting at this point are abnormal in that the form at the higher temperatures has the smaller volume.

$KHSO_4$ was suggested as a subject for investigation by a remark on page 95 of Groth's Chemical Crystallography. $KHSO_4$ forms with NH_4HSO_4 three series of mixed crystals, of different systems, only one of these being known as a possible form for the pure $KHSO_4$. It suggested itself that $KHSO_4$ might be really trimorphic. We have here, at higher pressures, other modifications as suspected, but they are four in number instead of only three. It would be most interesting to find whether either of the new modifications stable at high temperatures at atmospheric pressure is really of the same crystalline system as the mixed crystals of $KHSO_4$ and NH_4HSO_4.

Ammonium Acid Sulfate.— The reason for investigating this substance was the same as for $KHSO_4$, namely that the existence of other forms is suggested by the fact that under ordinary conditions these two substances form a series of mixed crystals belonging to three different systems. And as a matter of fact, just as in the case of $KHSO_4$, it is found that there are new forms at high pressures. However, there are, instead of the three forms suggested by the mixed crystal relations, demonstrably four forms, and I am morally certain that there is still another. Furthermore, the phase diagrams of $KHSO_4$ and NH_4HSO_4 show no obvious relation to each other. The relationship of isopolymorphism between the two substances must evidently be more complicated than is indicated by the mixed-crystals system at atmospheric pressure.

The substance used for this investigation was obtained from Eimer and Amend, and was of the "tested purity" grade. Two separate lots were used, which were practically identical in behavior. The analysis on the bottle showed only a minute trace of impurity. There was, however, considerable absorbed moisture. I removed this as far as possible immediately before use by keeping it in vacuum for six hours in the melted condition (at 160°). In spite, however, of the excellence of the analysis and the precautions to remove moisture, there was still a large amount of impurity left, judging by the lack of sharpness of the

freezing point. In fact, this is the most impure substance, judged by this criterion, for which I have ventured to publish data. At 150° it is entirely melted; at 139° it is mushy, perhaps $\frac{1}{10}$ melted, and even as low as 110°, it is perceptibly moist with the remnants of the melt. It may be of course that even the absolutely pure substance does not behave at the melting point like a simple substance; it might be, for example, that there is a reversible dissociation into something like $(NH_4)_2SO_4$ and H_2SO_4, although this precise dissociation is not likely.

Partly as a consequence of the width of the domain of melting, and partly as a result of the smallness of the change of volume, the data obtained for this substance are unsatisfactory in many respects. The

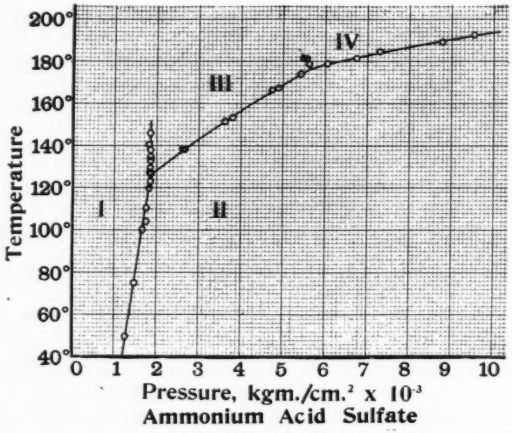

FIGURE 17. Ammonium Acid Sulfate. The observed equilibrium pressures and temperatures.

changes of volume are probably in error by large amounts. These changes as measured fall far short of satisfying the additive conditions at the triple point I–II–III. Furthermore, the additive conditions for ΔH are far from being satisfied at this point. The way in which the observed data should be adjusted so as to satisfy this condition does not readily suggest itself. I have preferred, therefore, not to try at all to deduce the latent heats and the changes of energy from the data, and in Table IX have tabulated only the equilibrium pressures

and temperatures and the sometimes very uncertain values for the changes of volume.

The phase diagram is shown in Figure 17, the measured changes of volume in Figure 18, and the numerical results in Table IX. The phase diagram itself may probably be accepted as substantially correct. The results could be repeated, and there was no rounding of the corners of the transition curves, making it unlikely that the impurity or chemical dissociation affects the transition pressures and temperatures. The approximate location of the melting curve may be estimated from the fact that points at higher temperatures than those shown on the lines I–III and III–IV were attempted, but were not possible because of the closeness of the melting.

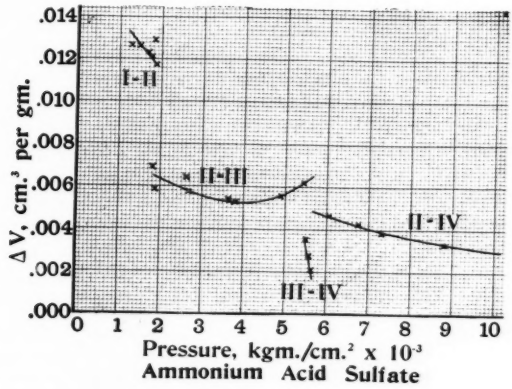

FIGURE 18. Ammonium Acid Sulfate. The observed differences of volume.

In addition to the phases shown, it is almost certain that the II–IV line should split at higher pressures with the appearance of a fifth phase. It was practically impossible to determine the exact location of the transition, because of the very small change of volume, but the existence of the transition was made practically certain in the following way. At room temperature pressure was raised to about 11000 and then temperature was raised to 198.5°, the pressure rising to something over 12000. Then the pressure was lowered at constant temperature, but I could find no point in the expected place (11200) on the II–IV

TABLE IX.

Ammonium Acid Sulfate.

Pressure	Temperature	ΔV cm³./gm.
	I–II	
1220	40°	.01330
1370	60	1295
1520	80	1259
1670	100	1224
1810	120	1188
	I–III	
1860	130°	.00529
1860	150	
	II–III	
2000	128°.4	.00635
3000	143 .4	555
4000	156 .9	524
5000	169 .3	569
	III–IV	
5650	177°.0	.00168
5530	181 .0	265
	IV–V	
6000	178°.3	.00466
7000	183 .1	406
8000	187 .1	360
9000	190 .6	325
10000	193 .8	300
	Triple Point, I–II–III	
1860	126°.2	
	Triple Point, II–III–IV	
5360	176°.9	

line. Thinking that by some careless oversight I might have run across the II–IV line while raising temperature, I lowered the temperature at 8000 to 140°, which is far enough to compel the transition from IV to II. This procedure was made necessary because on the transition line II–IV the superpressure required to force IV to change to II is so great that it cannot be reached in the limits of this work. The reverse transition, II to IV, however, runs with little transgression of the transition line. After lowering temperature to 140°, I then raised the pressure to 12000 and the temperature to 198.5°, the pressure rising to 12500. The rise of pressure accompanying this last change of temperature was larger than usual. Furthermore, as judged by the rise of pressure, the process of attaining temperature equilibrium extended over an unusually long interval of time, and then suddenly the supposed process of temperature equalization ceased. The result of all this manipulation was that, provided the II–IV line continues as it starts, the phase II must certainly have been in the apparatus at 12500 kgm. and 198.5°. Now on lowering pressure the transition to IV should have been found at about 11200. No such transition was found, however, down to 7500. The explanation, of course, that suggests itself is that the line II–IV does not continue as it starts, but encounters a triple point and splits into two. The apparent sluggishness in reaching temperature equilibrium was really due to the new transition. The point 12500 and 198.5° is therefore in the domain of the new phase, V, and the point at 7500 and 198.5° is doubtless in the domain of IV, the transition from IV to V not being noticed because of the smallness of the change of volume. This was verified by lowering temperature at 7500 from 198.5° to 181.6°, and then lowering pressure further. The transition IV–III was found in the location expected.

Figure 18, for Δv, requires some comment. The points on II–IV lie smoothly and normally, and the results are probably near the truth. The shape of the Δv curve for II–III is unusual in the marked rise on approaching the triple point II–III–IV. This rise, however, is consistent with the marked drop of Δv for III–IV with falling temperature. The rise and the drop both mean the same thing, that near the triple point the thermal expansion of III becomes unusually large. Furthermore, the curves for II–III, III–IV, and II–IV satisfy the additive condition at the triple point without forcing. It is probable that affairs are really as measured, and that III does increase markedly in expansion near the triple point. At the triple point I–II–III, however, the state of affairs was not nearly so satisfactory. The change of

volume on I–II was not so consistent as it should be, considering the rapidity and sharpness of the reaction. On the line I–III it was not possible to obtain any consistent measurements at all. Four measurements were made, which varied irregularly with temperature from 0.0032 to 0.0078. These points are not shown in the figure, and in the table the listed value was obtained from the conditions at the triple point. This value is evidently uncertain because of the lack of agreement of the two points on the lower end of II–III. Besides these four points, on the I–III line, the only other points not shown in the figure are two of the higher pressure points obtained with the first set-up with a patched cylinder, which later developed a perceptible leak.

The reaction velocity phenomena were as follows. On the line I–II the transition is rapid and easy to measure near the triple point, but becomes so rapidly slower with falling temperature that it did not pay to try for points below 50°. On the I–III line the transition is rapid, in both directions, but is strikingly more rapid with falling pressure. The transition II–III is slow over the entire length of the curve, but III–IV is rapid. It has already been mentioned that on the II–IV line the transition in the direction from II to IV runs easily, although very slowly, with falling pressure, but that the reverse transition from IV to II cannot be forced within the limits of the apparatus at the higher temperatures. About 5000 kgm. superpressure is necessary.

The unusually large error in the results makes it of no use to try for $\Delta\alpha$, $\Delta\beta$, or ΔC_p.

Since these other forms were not known before, there are no other values for comparison. Even the melting point is not listed; it is without doubt greatly affected by small quantities of moisture.

Figure 19 suggests the simplest conceivable mixed crystal diagram for $KHSO_4$ and NH_4HSO_4 at atmospheric pressure that will explain the three known series of crystals at room temperature. Whether this surmise is really correct or not cannot be verified until the crystalline forms of $KHSO_4$ at atmospheric pressure have been determined. But in any event, the possibility of so simple a diagram shows that there is no necessary connection between the new high pressure modifications of NH_4HSO_4 and those of $KHSO_4$. In fact, the entire dissimilarity of the phase diagrams shows that such a connection is not likely.

Cuprous Iodide.— Two lots of this material were used; the first was 55 gm. from Eimer and Amend, with which the existence of a transition was discovered, and the second lot was of 100 gm. from Hoffmann and Kropff, with which the final measurements were made.

It was hammered cold into an open steel shell, and pressure transmitted directly to it by kerosene.

There are two modifications; the transition is of the ice type, and within the temperature range of this work the second phase exists only at the higher pressures. The experimental values of pressure and

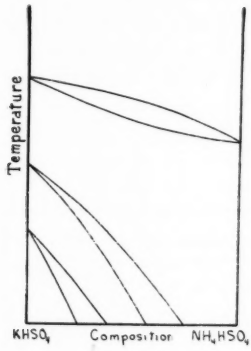

Fig. 19.

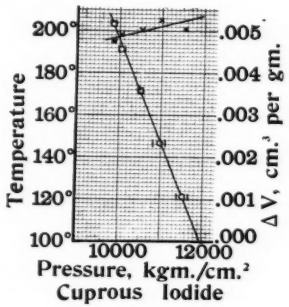

Fig. 20.

FIGURE 19. Possible mixed crystal diagram between Ammonium Acid Sulfate and Potassium Acid Sulfate.

FIGURE 20. Cuprous Iodide. The observed equilibrium pressures and temperatures (circles) and the observed differences of volume (crosses).

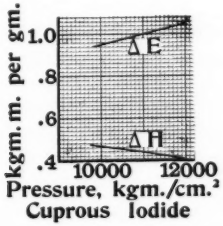

FIGURE 21. Cuprous Iodide. The calculated latent heat and the changes of internal energy.

temperature and change of volume are shown in Figure 20, the computed values of latent heat and change of internal energy in Figure 21, and the collected numerical results in Table X. The diagram seems normal in every way. This is one of the few examples found in this

investigation of a substance showing a new phase at 200° and not at 20°.

The transition is singular in that there is a region 150 to 250 kgm. wide within which the transition velocity is very slow, whereas outside of this band the velocity increases with unusual rapidity. At any given temperature the equilibrium point was found by artificially changing pressure until a point was found at which the pressure did not change by as much as 0.5 kgm. in 5 minutes. These stationary points are the equilibrium points shown in the diagram. Points were

TABLE X.

CUPROUS IODIDE.

Pressure	Temperature	ΔV cm³./gm.	$\frac{dT}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
11950	100°.0	.00535	−0.04926	.405	1.045
11544	120 .0	525	"	.419	1.025
11138	140 .0	515	"	.432	1.006
10732	160 .0	505	"	.444	.985
10326	180 .0	495	"	.455	.966
9920	200 .0	485	"	.466	.947

also found on each side of the equilibrium points at which the transition was perceptibly running in opposite directions. These points are also indicated in the diagram.

Within the limits of error the transition line is straight. It would extrapolate to a transition point at atmospheric pressure at 690°. The melting point of this substance is listed at 638°. Gossner [26] makes the statement that, on heating, the ordinary cubic form of Cu_2I_2 changes to a doubly refracting form. He does not state the temperature of transition, except to say that it is very high, but it must probably be considerably lower than 638° if the optical observa-

26 B. Gossner, ZS. Kryst., **38**, 110 (1903).

tion is to be possible at all. It is therefore improbable that the phase found above is the same as that mentioned by Gossner. There must be at least three modifications. From the meagre data at hand a phase diagram in its general features like that of AgI does not seem improbable.

The difference of compressibility can be determined in the usual way from the difference of slope of the isothermals above and below the transition. All five determinations gave fairly consistent results. The low temperature form is less compressible, and a fair average for the difference is 0.0_64 cm.^{3} per gm. per kgm. The measurements were not accurate enough to give the variation of this along the transition line. Using this value for $\Delta\alpha$, we may find as average values over the entire range for $\Delta\beta$, 0.00006, and for ΔC_p, 0.34 kgm. cm. (0.0014 gm. cal.). The high temperature form is the more expansible and has the higher specific heat. The relations of the two phases, so far as the signs of $\Delta\alpha$, $\Delta\beta$, and ΔC_p go, is exactly that of water and ordinary ice.

AMMONIUM IODIDE.— This substance has a new modification, which is striking because of the large change of volume, about 14%. The transition line runs steeply, with pronounced concavity toward the temperature axis, and crosses the line of atmospheric pressure at about $-17.6°$. It should, therefore, be comparatively easy to study this form under atmospheric conditions.

In all, three different sets of runs were made. The first set was for purposes of exploration. No transition at 20° was found between 12300 and 3500 kgm., and at 200° the only transition found up to 12300 was at approximately 2000. The second set included the measurements with the high pressure apparatus, and included all points between 20° and 200°. The material was from Hoffmann and Kropff, dried in vacuum before use, and hammered cold into the steel shell. Pressure was transmitted directly by kerosene. The third run with the low pressure apparatus, by the method of varying pressure at constant temperature, gave the point at 0°. The substance for this run was obtained from Eimer and Amend, and was used directly without any preparation. It contained slight traces of moisture, and judging from its light yellow color, it could not have been quite so pure as the previous sample.

The experimental values of pressure and temperature and of the change of volume are shown in Figure 22, the calculated values of the latent heat and the change of internal energy in Figure 23, and the numerical values are collected in Table XI.

At 200° the velocity of transition is very high, but it becomes less at

lower temperatures until at 50° the velocity is so low that a value of Δv too low was obtained, the reaction appearing to have stopped before it really had. At 25° an attempt was made to avoid this source of error by raising the temperature to 100° in the middle of the run to ensure completion of the transition, and then bringing it back again. The attempt seems to have been not entirely successful. At 0° the pressure was lowered to atmospheric pressure for an hour to ensure completion, with apparently satisfactory results.

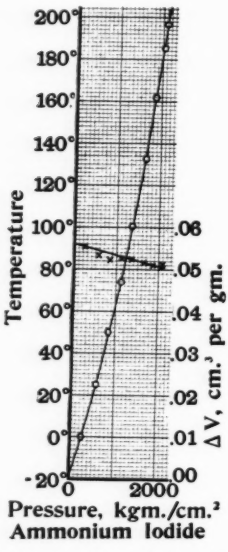

FIGURE 22. Ammonium Iodide. The observed equilibrium pressures and temperatures (circles) and the observed differences of volume (crosses).

At the two upper points of the curve there was a very slight rounding of the corners noticeable at the last reading, about 180 kgm. before the transition. The behavior was not like that usually found for an impure substance, and there is therefore a slight possibility that there may be a third phase, the transition line splitting in the neighborhood of 160° into two lines diverging at a very slight angle. If such is the case, the coördinates above are for the left hand of the two branches.

The amount of transgression of the transition line possible before the transition starts is a matter of 100 or 200 kgm. at the lower temperatures. A greater degree of subpressure than of superpressure may be supported.

The direct measurement of the difference of compressibility of the two phases did not give results so accurate as are sometimes obtained, but the conclusion is fairly safe that the difference is not greater than $\pm 0.0_5 1$ cm.³ per gm. per kgm. Using these limits for $\Delta\alpha$, we find fairly close limits for the quantities $\Delta\beta$ and ΔC_p when calculated in the usual way. Over the entire length of the curve both $\Delta\beta$ and ΔC_p are negative on either assumption for $\Delta\alpha$; that is, the high temperature phase is less expansible and has the lower specific heat. At 100 kgm. (−8°) $\Delta\beta$ lies within the limits $-0.0_4 26$ to $-0.0_4 54$ cm.³ per gm. per degree Centigrade, and ΔC_p between −0.023 and −0.026 cal. per gm. At 2053 kgm. (190°) the limits of $\Delta\beta$ are $-0.0_5 8$ to $-0.0_4 21$, and for

ΔC_p −0.013 to −0.014. The closeness of these limits for ΔC_p is unusual, and we may accept the value with some confidence.

It is interesting that the existence of a second modification has been suspected by a number of observers because of the behavior of the mixed crystals with NH_4Br and NH_4Cl. In fact, Wallace [27] made a search down to −16° without result; if he had gone only two degrees farther he would have found what he was looking for.

Ammonium Bromide.— This was obtained from Eimer and Amend, U. S. P. Before use it was dried in vacuum at 100°. Whatever impurity there may be present does not form mixed crystals and so affect the transition point, because the transition was always very sharp and rapid, with no rounding of the corners whatever. Very little transgression of the transition line is possible before the transition starts; the maximum observed was a superpressure of 30 kgm.

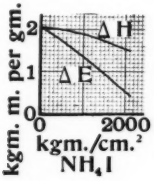

Figure 23. Ammonium Iodide. The calculated latent heat and the change of internal energy.

The equilibrium pressure was shut within limits which were usually 3 kgm. apart, and in the extreme case only 6 kgm. apart. The transition line is very steep; it runs from about 138° at atmospheric pressure to 680 kgm. at 200°. All the measurements had, therefore, to be made with the low pressure apparatus. Two sets of readings were made with the same sample. The repetition was necessary because the first set of Δv points was irregular. There seems to be some sort of internal strain set up by the transition which it is necessary to remove by seasoning. For the second run the transition was carried backward and forward a number of times before any measurements were made. The agreement of the pressure-temperature points of the two runs was very close. The substance was placed in the open steel shell, and pressure transmitted to it by kerosene.

The observed equilibrium points and the changes of volume are

27 R. C. Wallace, C. Bl. f. Min. 1910, p. 33.

shown in Figure 24, the computed values for the latent heat and the change of internal energy in Figure 25, and the numerical values are collected in Table XII. Both sets of pressure-temperature points are shown, but only the Δv values of the second set of determinations. The direction of curvature of the transition line, convex toward the pressure axis, is noteworthy. It is in the same direction as for NH_4I.

It was known previously that NH_4Br has a second modification. Its existence was first suspected from the behavior of the mixed crystals with NH_4I, and was afterward established by Wallace [27] by

TABLE XI.

AMMONIUM IODIDE.

Pressure	Temperature	ΔV cm³./gm	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	−17°.6*	.0561*	.0699*	2.05	2.05
245	0 .0	554	748	2.02	1.89
503	20 .0	547	807	1.99	1.71
742	40 .0	540	870	1.94	1.54
964	60 .0	534	938	1.89	1.38
1171	80 .0	528	.1012	1.84	1.22
1362	100 .0	523	.1096	1.78	1.07
1537	120 .0	518	.1189	1.71	.92
1698	140 .0	514	.1287	1.65	.78
1848	160 .0	510	.1388	1.59	.65
1988	180 .0	507	.1490	1.54	.54
2118	200 .0	504	.1593	1.50	.43

microscopic examination. No satisfactory measurements of the physical constants are extant, however. Wallace was able to state only that the high temperature modification has the larger volume. Not only is this true, but the change of volume is one of the highest known for solids. That Wallace did not comment on this shows the difficulty of making quantitative estimates of the change of volume from any alteration of appearance. I can verify this from my own experience. The transition temperature found by Wallace was 159° against 137.8° above. There would seem to be no question but that

* Extrapolated.

the lower value is the more accurate, when one considers the contrast in the methods. The lower value was obtained with both phases in contact, and is the average of results differing only 3 kgm. for opposite directions of the transition. Wallace's value was obtained with

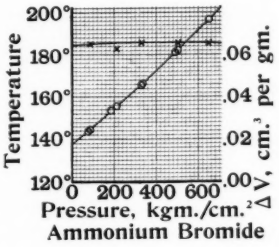

Fig. 24.

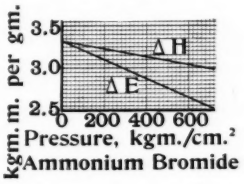

Fig. 25.

FIGURE 24. Ammonium Bromide. The observed equilibrium pressures and temperatures (circles) and the observed differences of volume (crosses).

FIGURE 25. Ammonium Bromide. The calculated latent heat and the change of internal energy.

TABLE XII.

AMMONIUM BROMIDE.

Pressure	Temperature	ΔV cm³./gm.	$\frac{dT}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm
0	137°.8	.0647	.0800	3.32	3.32
100	146 .0	652	834	3.28	3.21
200	154 .5	656	869	3.23	3.10
300	163 .4	659	903	3.18	2.99
400	172 .4	660	937	3.14	2.87
500	181 .9	659	972	3.09	2.76
600	191 .8	658	.1006	3.04	2.65
700	202 .0	655	.1040	2.99	2.53

the microscope, in which temperature control is not so easy, and was not an equilibrium measurement between two phases simultaneously present. I have already stated that the character of the transition rules out the possibility of there having been any effect exerted by impurities on the data given here.

AMMONIUM CHLORIDE.— This was Kahlbaum's purest, and was dried in vacuum at 100° before using. Its behavior is very similar to that of NH_4Br. The transition line is also steep, and the transition temperature at atmospheric pressure is higher than that of NH_4Br. All the measurements were made in the low pressure apparatus, and only three points were determined, up to 203° and 275 kgm. The reaction is just as sharp as for NH_4Br, and the pressure limits no wider; in fact it would be difficult to imagine two substances more alike in the character of the transition.

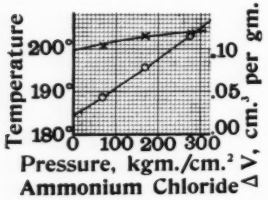

Fig. 26.

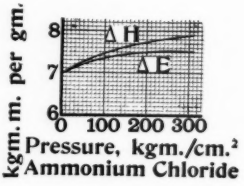

Fig. 27.

FIGURE 26. Ammonium Chloride. The observed equilibrium pressures and temperatures (circles) and the observed differences of volume (crosses).

FIGURE 27. Ammonium Chloride. The calculated latent heat and the change of internal energy.

The observed equilibrium pressures and temperatures and the changes of volume are shown in Figure 26, the computed values of the latent heat and the change of internal energy are shown in Figure 27, and the numerical values are collected in Table XIII. The transition curve is distinctly convex downward, as it is also for NH_4I and NH_4Br. The Δv curve is concave downward. Such is also the case for NH_4Br, but in the case of NH_4Cl the Δv curve has not yet reached the maximum in the range shown, whereas the corresponding curve for NH_4Br does pass through a maximum in the range of the experiment.

It has been known previously that NH_4Cl also has a second form at high temperature which has a greater volume than the low temperature form. Wallace [27] gives 159 ° for the transition point, against 184.3° above. There is no previous measurement of ΔV.

Further comment will be made on the behavior of these three halogen compounds under the discussion by groups. This is the best example of a thorough going isopolymorphism that I have found.

THE ANTIMONY SULFIDES.— Antimony may form either the trivalent or the pentavalent sulfide, Sb_2S_3 or Sb_2S_5. Sb_2S_3 exists in two distinct modifications; a black form occurring in nature, and a red form, said to be amorphous, which is formed chemically by precipitation. The red modification may be changed to the black at atmospheric pressure by heating to about 200°. Sb_2S_5 has also apparently two forms; the commercial form is a bright orange powder, but when made in the laboratory by precipitation with H_2S from solution it is

TABLE XIII.

AMMONIUM CHLORIDE.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
0	184°.3	.0985	.0645	6.98	6.98
100	190 .9	.1087	675	7.47	7.36
200	197 .8	.1160	705	7.73	7.50
300	205 .0	.1212	735	7.88	7.52

red in color, very much like the red Sb_2S_3. The materials used in this investigation were obtained from two sources; the black Sb_2S_3 and the orange Sb_2S_5 were from Eimer and Amend, and the red Sb_2S_3 and red Sb_2S_5 were made especially for me at the Chemical Laboratory of Harvard University.

The behavior of Sb_2S_3 will be first described. The black modification shows no peculiarity; there is no new form to 12000 at 20° or 100° or 200°. The red Sb_2S_3 changes to the black Sb_2S_3 on heating in a peculiar way. Up to temperatures of 150° and pressures up to 12000 kgm. no change in the red is produced; this was verified by taking the apparatus apart after exposure to these values. If red Sb_2S_3 is heated at 12000 kgm. however, some sort of change takes place between 150° and 200° accompanied by a decrease of volume. If after exposure to 200° at 12000 kgm. the apparatus is cooled, still under 12000 kgm.,

and then opened, it will be found that the change from red to black Sb_2S_3 has not taken place completely; the mass is mostly transformed, but there is still an appreciable quantity of the red left throughout the mass, and particularly on the surfaces. The complete transition from red to black Sb_2S_3 (which of course is irreversible) takes place in two stages; the first stage is as just described at a pressure of 12000 kgm. somewhere between 150° and 200°, and the second stage takes place on releasing pressure from 12000 kgm. at the constant temperature of 200° at a pressure of about 10000 kgm. This second stage in the transition is also accompanied by a drop of pressure, that is, by a decrease of volume. I have verified by trial that this second stage in the decomposition is irreversible, as indeed it must be. This second drop is remarkable; if the second stage in the transition were purely a pressure effect, thermodynamics shows that it must be accompanied by an increase of volume, instead of a decrease. The observed effect must be due to friction; the highest pressures so increase the frictional resistance to the second stage of the transition that it cannot run, but as pressure decreases the frictional resistance falls rapidly until it is low enough for the transition to proceed.

In addition to the irreversible change to the black Sb_2S_3 at high temperatures, red Sb_2S_3 shows a reversible transition at lower temperatures. Several measurements of this reversible transition were made. The transition line runs from 7800 kgm. at 0° to 12000 kgm. at 32°, and the change of volume is approximately 0.010 cm.^{3} per gm. It was not possible, however, to make any very accurate measurements of this transition. The reaction is sluggish, and there is some impurity present, as shown by the rounding of both corners of the Δv curves, an unusual feature. It seems that it is not possible to obtain Sb_2S_3 entirely pure, but it always contains some free S and Sb_2S_5 and other sulfides. The result above shows that this impurity is soluble in both phases. It is not likely, therefore, that any chemical refinement would give a much more satisfactory material, and I did not try for further more accurate measurements on the transition curve.

The importance of the existence of this second modification of red Sb_2S_3 is to be insisted on, however, because it shows that ordinary red Sb_2S_3 cannot be amorphous, but must be crystalline. No substance is known with a transition of an amorphous phase. The universal opinion that Sb_2S_3 is amorphous is doubtless due to its appearance, which is as a precipitate, too fine to show any crystalline structure. Tammann, however, states that amorphous red Sb_2S_3 may be obtained by rapidly cooling the melt of black Sb_2S_3. We see

now, however, that the subcooled red Sb_2S_3 cannot be a glass, but is another crystalline modification formed from the subcooled melt.

The system of the two modifications of Sb_2S_3 now becomes strikingly like that of red and white phosphorus. Red Sb_2S_3 corresponds to white phosphorus, and black Sb_2S_3 to red phosphorus. Red phosphorus and black Sb_2S_3 are both the absolutely stable forms, but there is frictional resistance to change so that the unstable forms will not change to the stable forms, even when inoculated, at low temperatures. The unstable white phosphorus and the red Sb_2S_3 furthermore each have a second modification, and the transition curves to these new modifications are very similar in location for the two substances. A careful study of the system Sb_2S_3 would be interesting, both for its own sake, and for the light which it might throw on the vexed question of the relation of the forms of phosphorus.

The results obtained with the two forms of Sb_2S_5 are curious and interesting, but have little real value because it is not possible to produce an Sb_2S_5 which is even approximately pure; the pure substance probably does not exist, but spontaneously decomposes into other sulfides and free sulfur. I have found the statement that under usual chemical methods of manufacture 40% of Sb_2S_5 is a high proportion. The behavior of the two specimens of Sb_2S_5 becomes intelligible from this point of view. The red modification is one in which there is a large proportion of red Sb_2S_3. At low temperatures it shows the same transition as the red Sb_2S_3, but with corners considerably more rounded, and the transition is at a somewhat higher pressure. This is as one would expect as the result of an increased proportion of dissolved impurity. On heating to 200° under a pressure of 12000 kgm. and then releasing pressure at 200°, decomposition takes place of what Sb_2S_5 there is to black Sb_2S_3 and free S. At approximately 4000 kgm. and 200° the melting point of the free S is reached. This gave the appearance of some sort of a new transition until the true nature of the effect was discovered. The presence of free sulfur may be easily proved by digesting with CS_2, or in some cases acicular crystals of sulfur several mm. long were formed. The melting point of the sulfur is much rounded, showing that the Sb_2S_3 is soluble in sulfur, as one might expect. The appearance of the Sb_2S_3 remaining after the decomposition is black, exactly like that of red Sb_2S_3 subjected to the same treatment. It is noteworthy that the decomposition in two stages, particularly the decrease of volume at 10000 kgm. at 200° could not be detected.

The orange Sb_2S_5 behaves as if it contained a larger proportion of

Sb_2S_5. At room temperature it shows no transition at all to 12500 kgm.; probably the impurity of Sb_2S_3 is so effectively dissolved in the other components that its transition is suppressed. On raising temperature at 12000 on the orange Sb_2S_5 a partial decomposition takes place with decrease of volume, and on releasing pressure at 200° the decomposition is completed near 5000 with further decrease of volume. This second point at 5000 was verified by repetition with another sample. On further release of pressure to 4000 the melting point of the free sulfur is reached. The end product is free sulfur and black Sb_2S_3, just as in the previous case. It is curious that the manner of decomposition of the orange Sb_2S_5 should be more like that of the red Sb_2S_3 than that of the red Sb_2S_5, although the latter doubtless contains a larger proportion of red Sb_2S_3 than the orange Sb_2S_5. The most obvious difference between the decomposition of red Sb_2S_3 and orange Sb_2S_5 is that with the latter the decrease of volume at 200° occurs at a considerably lower pressure, 5000 against 10000. Probably the explanation is partly to be found in complicated mixed crystal relations.

No further attempt was made to straighten out the relation of these various sulfides; a complete investigation would be a matter of great difficulty, demanding first of all accurate chemical analysis of the various substances. As such, the subject is beyond the scope of this investigation.

Double Sulfate of Zinc and Potassium. $[K_2Zn(SO_4)_2]$.—This was obtained from Eimer and Amend. Analysis showed Fe, .0004%; Na, none; chloride, none. The salt crystallizes from solution with six molecules of water. In this form it shows no new modification to 12000 kgm. at 20° or 100°. The substance was also examined in the anhydrous condition; the water was removed by heating in vacuum to 140° for $1\frac{1}{2}$ hours. The anhydrous salt also has nothing new to 12000 at room temperature, but does have a transition at higher temperatures. The transition is well marked. Figure 28 shows the relation between pressure and temperature. The general order of magnitude of the change of volume is 0.015 cm.^{3} per gm., but there were various irregularities. Once or twice an appearance was found as of a second small transition like a satellite of the main transition. The curves of volume against pressure at constant temperature present an appearance which one might at first take for the usual rounding in the presence of an impurity, but more careful reading shows not a rounding but a sharp break in the direction of the isothermal above the main transition. This is shown in Figure 29.

In view of the known chemical behavior of such double salts, there seems little question as to the proper interpretation. We have here not a polymorphic transition in the proper sense of the word, but a reversible decomposition of the double salt into two simple salts. The decomposition is further complicated by the formation of mixed crystals between the various products. The correctness of this surmise would be at once verified if the extrapolated transition at atmospheric pressure agreed with the known temperature of decomposition. I have not been able to find, however, that this point has ever been determined; the decomposition point of the hydrous salt is well known, but no work seems to have been done on the anhydrous salt.

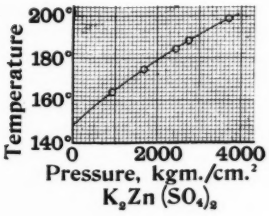

Fig. 28.

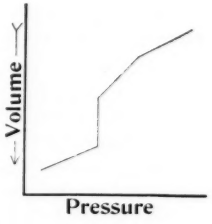

Fig. 29.

FIGURE 28. Zinc Potassium Double Sulfate. The observed equilibrium pressures and temperatures. This transition is probably a decomposition of the double salt into two simple salts.

FIGURE 29. Zinc Potassium Double Sulfate. Shows the general nature of the change of volume.

If this explanation is correct, it removes this substance at once from the range of this work, and I did not try for further data. It is obvious, however, that there is here an immense field, as yet untouched. For instance, it would be of great interest to examine the other double sulfates of this series. The careful work of Tutton shows that the hydrous salts of the series present remarkable similarities. I am not aware that any measurements have ever been made on the decomposition of double salts, or on mixed crystals, under pressure. The work above showed that accurate measurements on mixed crystal equilibria under pressure is going to involve very tedious manipulation, because diffusion takes place so slowly.

THALLIUM.— This substance was procured for the purpose of making the nitrate from it; the measurements on the pure metal were under-

taken only because it happened to be on hand, and because it is known to be polymorphic. Only a small quantity was available; I procured all there was to be obtained in this country — 3 ounces from Merck and 2 ounces from Eimer and Amend. This was only a quarter of the amount required to fill the apparatus.

The transition point at atmospheric pressure to the second modification is known to be at about 225°, and the transition is of the ice type. The effect of pressure has been investigated by Werner [28] up to 3000 kgm. He found that the slope of the transition line is only $-2°$ for 1000 kgm., and that the change of volume is excessively small, much too small to allow accurate measurements in the present apparatus with the small quantity of material available. It should, however, be easy to detect the presence of the transition. The particular interest of this present examination is in finding whether there is not a third modification, giving a diagram like that of AgI. The change of volume to this third modification would be larger than that between the two known forms and should be readily detectible if present. The principal result obtained by my work is that there is no third modification up to 12000 at 200°. At higher temperatures the presence of the transition line investigated by Werner could be detected, and his conclusions verified within my wide limits of error. My data are not inconsistent with his value for the slope of the curve, and my value for the change of volume agrees with his at 2500 kgm. My data do not indicate, however, the unusually large increase of Δv found by him toward the high pressure end of the line, but would indicate approximate constancy of Δv. The pressure limits of indifference to the transition are wide, and become rapidly wider at the higher pressures. Werner's data indicate the same thing, although his measurements were made with increasing temperature at nearly constant pressure, whereas mine were made at constant temperature.

Ammonium Potassium Phosphate $[(NH_4)_2KPO_4]$.—This substance was obtained from Eimer and Amend, "tested purity," and showed Cl 0.0005%, Fe 0.0002%, with traces of SO_3 and CaO. It crystallizes with four molecules of water. For this experiment the water was removed by heating to 100° in vacuum for two hours. The dried salt was then hammered cold into an open steel shell, and pressure transmitted directly to it by kerosene.

There is a transition to a new form at high pressures and at temperatures in the neighborhood of 100°, but in this vicinity the substance is

[28] M. Werner, ZS. anorg. Chem., **83**, 275 (1913).

apparently unstable, so that it was not possible to make any accurate measurements. About all that I could do was to determine the general character and location of the transition. Two runs were made. The first was an exploring run; it showed the existence of a new modification with a transition near 11000 kgm. at 100°. No transition was found at room temperature to beyond 12000. Presumably, therefore, the transition is of the ice type. The second run, for purposes of measurement, verified the existence of the transition, and gave for the more accurate coördinates at 100°, 11480 kgm., with a change of volume of about 0.0035 cm.^{3} per gm. Temperature was then lowered to 86°, and the transition pressure found to be at least as high as 11800, verifying that the transition is of the ice type. The apparatus was now left over night. The next morning at 128°, instead of one transition point, two were found, at 9600 and 8900 kgm. The transition line has split, and there are three modifications. But a disquieting fact was that the total change of these two new transitions was less than half that found for the single transition the day before. These two transitions were verified by repetition. Temperature was now raised to 141°, and again two transitions found at still lower pressures, at very roughly 8000 and 8700. The apparatus was again allowed to rest, this time over Sunday. On Monday morning temperature was raised to 90° and pressure to 12500, preparatory to a run. It took an unusually long time to reach pressure equilibrium, the pressure continuing to drop. After approximate equilibrium had been reached, no trace of the transition was to be found within 1800 kgm. of the previous location, and again on raising temperature to 100° the transition had entirely disappeared.

The evident explanation of these effects is that $(NH_4)_2KPO_4$ has three modifications, with transition coördinates approximately as given. But in the region in which the transition runs the substance is itself chemically unstable, and gradually changes to some other substance with decrease of volume. The fact that the change of volume is a decrease shows that the instability has been brought about by the high pressure and not by the high temperature. The change is not accompanied by change of color, nor setting free of NH_4, to judge by the lack of odor.

It is unfortunate that the decomposition does not allow closer study of these transitions, because they are of a rather rare type. At the triple point it seems that three lines, all of the ice type, come together. The only previous example of this is $KHSO_4$.

It is quite possible that the decomposition is a splitting up into two

simple salts, as suspected for $K_2Zn(SO_4)_2$. The apparent irreversibility may be simply an effect of diffusion, which must be very slow at high pressures.

Potassium Binoxalate. — This was obtained from Eimer and Amend. It was hammered cold into the open steel shell, and pressure transmitted directly to it by kerosene. It crystallizes with one molecule of water. This, like $(NH_4)_2KPO_4$, is a substance with a new modification in a region where it is chemically unstable, so that it was not possible to more than establish the existence of the transition. The instability is greater than that of $(NH_4)_2KPO_4$. At room temperature no transition was found to 12000. At 100°, there is a transition at about 8000 kgm., with a change of volume of about 0.0009 cm.^{3} per gm. This transition was verified by repetition. Presumably it is of the ice type. On setting up the apparatus again, no transition could be found at 100°, nor yet at 200°. On cooling and opening the apparatus there was an almost explosive evolution of gas, and the substance was found completely decomposed. For some reason the decomposition must have taken place at a temperature lower than 100° on the second run.

General Survey of all Substances Examined.

The purpose of this section is two-fold. It is, first, to give a list of all those substances among which I have made unsuccessful search for other modifications. Information of this sort is doubtless of value, but too much weight must not be attached to it because failure to find a new form does not prove that none is capable of existence — the frictional resistance to the transition may be too great to allow it to start. In the second place, the purpose is to give some idea of the nature of the clues that I have followed in the attempt to coördinate the various data and to find some method of predicting whether a given substance is likely to have new polymorphic forms. This purpose will be served by grouping the various substances according to the clue that suggested their investigation. This purpose will also be furthered by including in the groups the substances which do have new forms and the data for which I have already published. The following contains, therefore, a collection by groups of all the substances that I have investigated either for melting or polymorphic forms. Of course for those substances whose melting curves have been measured, the range over which search for polymorphic forms

has been made is of necessity more restricted than for the other substances. Since the same substance has sometimes been suggested by more than one clue, cases will be found of the inclusion of the same substance in more than one group.

The search for new modifications has been made, unless stated to the contrary, up to 12000 or 13000 kgm. at 20° and 200°. For substances melting within the range, search was made out to 12000 at room temperature and the highest temperature of the melting curve. I have not especially mentioned these cases. If no transition is found on either of these isothermals, and if it is certain that there is no transition at atmospheric pressure between 20° and 200°, it is very unlikely that there will be found to be a transition at any pressure less than 12000 at any temperature between 20° and 200°. Benzol shows the character of the transition curves of possible exceptions. I have not, except in a few cases, made any examination for polymorphism at atmospheric pressure between 20° and 200°, but have accepted the absence of any mention in the literature of polymorphism as probable evidence that there are no other forms. In several cases, however, I have found forms at atmospheric pressure not previously listed. But it is very probable that if there is a transition at atmospheric pressure the transition line will run across the isothermal at either 20° or 200°, and so be discovered by the run to high pressures. It is not probable that any large transitions have been overlooked. Another restriction to which this investigation is subject is that the change of volume of the transition must be large enough to detect with this apparatus. It is not likely that transitions with a change of volume of much less than 1/100% would have been detected, although if the transition were known to exist, measurements could be made on still smaller transitions. This means that transitions as small as many described by Cohen [29] in his papers on the allotropy of the metals are beyond the reach of this apparatus.

It will pay to give a preliminary discussion of the nature of the various clues. The clue of chemical similarity is perhaps the most obvious of all. If one substance shows polymorphism, one may expect others built up on the same chemical scheme also to have polymorphism. The expectation is especially strong if the substances differ only by the replacement of one element by another which usually stands to it in the relation of isomorphism. In particular the substitution of one atom for another would be expected to have less disturb-

29 Ernst Cohen, Proc. Amst. Acad., numerous papers in 1914 and 1915.

ing effect on polymorphic relations when it takes place in a complex than in a simple molecule. Evidently crystalline form is an important factor in the matter of chemical replacement; the chances are much greater for polymorphic similarity in those cases where the known forms belong to the same systems. In the following list of substances the crystalline system is given in all those cases where it is known.

There are some cases where the existence of mixed crystals suggests the existence of other forms. If one salt, A, crystallizes isomorphously with another, B, in a form which pure A does not show, then one may expect that possibly this strange form may correspond to a modification of A stable at higher pressures.

Salts with water of crystallization might possibly be expected to show other forms under pressure, since the water molecules are a much less tenacious part of the compound and might be compelled to assume new bonds by the high pressure. Similar reasoning suggests that possibly double salts will assume other forms under pressure.

Substances which crystallize in unstable forms from the melt, like a number of organic compounds, would seem to be promising material, because the molecules are known to have the capability of being built up into several arrangements. In the same way, one might hope for polymorphism among those inorganic compounds which are known to exist in several forms as minerals, but whose relationship of monotropy or enantiotropy is not known. And with some plausibility one might expect that in some cases the transition lines of substances with transitions at higher temperatures than 200° at atmospheric pressure might be brought down by pressure to the region of this investigation.

Finally a suggestion may be mentioned growing out of Tammann's [30] theory of polymorphism. He has suggested that according to his theory there is a particularly good chance of polymorphism among those substances whose melts are associated. It is known that most organic acids are associated in the liquid, and accordingly one would expect frequent polymorphism here. A number of this class of substances were investigated.

In the following, the substances investigated under each group will be first of all simply enumerated, those showing polymorphic forms being marked with an asterisk. In the text comments are made on the various substances as they are called for.

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30 G. Tammann, Gött. Nach., 1912, p. 1.

Chemically Related Groups.

(1) NITRATES.— KNO_3*, I trigonal, II rhombic; NH_4NO_3*, I cubic, II tetragonal, III monoclinic, IV rhombic, V tetragonal; $CsNO_3$*, I cubic, II trigonal; $RbNO_3$*, I trigonal, II cubic, III trigonal; $TlNO_3$*, I cubic, II trigonal, III rhombic; $AgNO_3$*, I trigonal, II rhombic; $NaNO_3$, trigonal; $LiNO_3$, trigonal, rhombic, cubic; $HgNO_3$; $Hg(NO_3)_2$; $Pb(NO_3)_2$ cubic, monoclinic; $Al(NO_3)_3$. This group has already been sufficiently commented on in a previous paper. The results are given again here for the sake of completeness and convenience of reference.

HALOGEN COMPOUNDS.— CCl_4*, CBr_4*, I cubic, II monoclinic; $SiCl_4$; C_2Cl_6*, I cubic, II triclinic, III rhombic; HgI_2*, I rhombic, II tetragonal; Hg_2I_2; AgCl, cubic; AgBr, cubic; AgI*, I cubic, II cubic quasi-hexagonal; NH_4Cl*, I cubic, II cubic; NH_4Br*, I cubic, II cubic; NH_4I*, I cubic, II cubic; TlI*, I cubic, II rhombic; KI, cubic; NaI, cubic; LiI; Cu_2I_2*, cubic; SbI_3, trigonal. It seems to be a general rule in the case of halogen compounds that compounds formed by the substitution of one halogen for another crystallize isomorphously, although there are exceptions. The effect of the substitution, in case the substance is polymorphic, is to displace the temperature of transition.

CCl_4 and CBr_4 each have three forms and might at first glance seem to be a very good example of isopolymorphism. But this relation is probably illusory, because the general character of the phase diagrams is so different, one being the inverse of the other. The crystalline form of ordinary CCl_4 seems not to be known, so that we cannot say whether the ordinary modifications of CCl_4 and CBr_4 correspond or not.

Possibly $SiCl_4$ may show other forms at lower temperatures and higher pressures than those reached here, in analogy with CCl_4, because in many compounds an atom of silicon is capable of replacing an atom of carbon. The expectation need not be very strong, however, because the physical properties of corresponding Si and C compounds are often very different, SiO_2 and CO_2 for example.

Other compounds analogous to C_2Cl_6 are known to be polymorphic, and it would be most interesting to examine them under pressure. These are $C_2Cl_4Br_2$, $C_2Cl_2Br_4$, C_2Br_6. Preparation of them was beyond my chemical resources.

HgI_2 is unique among all substances so far examined in that its

transition line has a maximum temperature. $HgBr_2$ under ordinary conditions has a form isomorphous with the high temperature form of HgI_2, while the form of $HgCl_2$ is not isomorphous with either the iodide or the bromide. It would be interesting to try the effect of pressure on the bromide and the chloride.

Hg_2I_2 is a substance listed in the Tables of the French Physical Society as dimorphous enantiotropic, with a transition point at 70°, on the authority of Yvon, in 1873. I have been unable to find the reference, but there is later work by Varet.[31] He recognizes three forms in all, but probably two of these forms are unstable and there is no enantiotropic transformation point. One variety is yellow-green; it is precipitated under some conditions, but is very unstable. The other new variety is red; it is unstable under ordinary conditions. The reaction from the ordinary yellow to this begins at about 70°, but is not complete until 245° is reached. It does not seem to be a transition of the ordinary type. In the present work, no new form was found up to 12000 kgm. at room temperature, or to 13000 at 125°. In a further search for the second modification, Hg_2I_2 was heated in a dilatometer at atmospheric pressure. Between 57° and 83° there can be no discontinuity of volume of so much as one part in 3000. The only evidence that I have found for the transition is a fairly rapid deepening of the yellow color to a brown, on heating through 70°. This evidence cannot be regarded as sufficient, however.

AgCl and AgBr are cubic and crystallize isomorphously with each other and the high temperature modification of AgI. We would expect therefore to find at low temperatures at atmospheric pressure a transition of each of these substances to another form isomorphous with the low temperature modification of AgI. No such transition point seems to be known, and I do not know whether the search has been made. Analogously one would expect at higher pressures at room temperature to find another modification of AgCl and AgBr corresponding to AgI (III). No such form was found, however, nor was there anything at 200°. In my previous paper I referred to the low temperature modification of AgI as hexagonal. There are many authorities for this, but the most recent work [32] seems to establish that this is cubic, although imitating very closely the hexagonal form by its peculiar method of twinning.

The series of three salts NH_4Cl, NH_4Br, and NH_4I, is the most

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31 R. Varet, Ann. Chim. Phys., **8**, 79 (1896).
32 F. Wallerant, Cristallographie, p. 275.

noteworthy example of any that I have found of complete isopolymorphism. Not only are the three substances so similar that they will form mixed crystals with each other, but the three phase diagrams of the pure substances are very similar, except for the absolute value of the temperature of transition at atmospheric pressure. These cases of polymorphism are also unique in another particular; the high and low temperature forms of each substance belong not only to the same crystalline group, the cubic, but also to the same sub-group, the pentagonikositetrahedric.

In large features the phase diagrams are much similar; the transition lines are unusually steep, the changes of volume are unusually large, the curvature of all three lines is unusual in that they are convex toward the pressure axis, and the transitions are all sharp and rapid with a very narrow band of indifference. In finer detail, however, the several diagrams do not show regular variations. The atomic weights of Cl, Br, I are approximately 35, 80, and 127. Br is very nearly half way between Cl and I and we should expect the properties of the NH_4Br transition to be midway between those of NH_4Cl and NH_4I. This regularity does not exist. The transition temperatures at atmospheric pressure are 184.3°, 137.8°, and −17.6°, in order of increasing atomic weight. The Br salt is much nearer the Cl end. It is noteworthy that the order of these transition points is the exact reverse of the usual order of the boiling or melting points of homologous halogen compounds — the chlorine compound having the lower boiling point and behaving as if it had less internal cohesion. The slopes of the transition lines at atmospheric pressure do not even follow the order of atomic weight, being 0.0645, 0.0800, and 0.0699. At the same temperature, however, the order is normal, being at 185°, for example, 0.065, 0.098, and 0.153. Again Br is nearer the Cl end. The changes of volume at atmospheric pressure are 0.0985, 0.0647, and 0.0561 cm.^{3} per gm. In this respect Br falls nearer the I end. The changes of volume per gm. molecule, which afford perhaps a juster comparison, are 5.26, 6.34, and 8.14. Br is now much closer to Cl. It is rather surprising that the molecular changes of volume of all three salts are not more nearly equal; the easy isomorphism would lead one to expect it. Finally, the latent heats of transition are 6.98, 3.32, and 2.05 respectively in kg. m. per gm., or 374, 327, and 247 kg. m. per gm. mol. According to the first method of comparison Br is closer to I, but by the second, which is more significant, is closer to Cl.

TlI is marked with an asterisk because it is known to have two modifications. The transition takes place on heating to about 168°,

and is well marked by the striking change of color, from yellow to red. I was not able, however, to make any measurements under pressure, or even to detect the transition, although I made careful search at 20°, 130°, and 200°. The explanation is to be found in the great sluggishness of the transition, which is much worse in this respect than HgI_2. Gernez [33] has found at atmospheric pressure that the yellow modification may be heated to 200° without initiating the transition, and that the red may be cooled to liquid air without starting the reverse transition. He has kept the unstable red modification for two years at room temperature without the transition starting. Furthermore he finds that the transition from one phase to the other is always slow, even when inoculated. The material is evidently unsuitable for experiment under high pressures. The only possibility is in finding some catalytic agent that will hasten the transition.

KI is cubic and isomorphous with the ordinary modification of NH_4I and the high temperature modifications of NH_4Br and NH_4Cl; it is strange that it showed no new form. KBr and KCl are also isomorphous with KI; judging by analogy with the ammonium salts one would might expect that these two would be more likely to show a new transition than the KI. They should be tried. KI is a substance for which Spring [34] announced a large permanent change of volume after exposure to 10000 kgm. at room temperature. I could find no evidence for it.

NaI is not isomorphous with KI, but it is with AgI. One would expect new forms.

LiI crystallizes with three molecules of water, the "melting point" at atmospheric pressure being at about 72°, at which it gives up two molecules of water. At 200° this transition point was found displaced to about 10000 kgm. with a change of volume of approximately 0.015 cm.^{3} per gm. It is a matter of considerable difficulty to produce anhydrous LiI, and I did not make the attempt.

SbI_3 has been erroneously described as having enantiotropic transition points; it has already been discussed under melting.

Among other compounds of this class which could be profitably examined is PbI_2: this is known to have a transition at atmospheric pressure, but at a temperature so high as to be beyond the range of this work.

Summarizing the behavior of the halogen compounds, polymorphism

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33 D. Gernez, C. R., **138**, 1695, 1904, and **139**, 278 (1904).
34 W. Spring, Rap. au Cong. international Phys., **1**, 402 (1900).

seems to be of frequent occurrence in this group, but except for the three ammonium salts, the phase diagrams of the various salts have no relation whatever to each other. The frequency of polymorphism cannot be ascribed to any detailed resemblance in the structure of the crystals of the several salts, but must be due to some rather general property of the halogen elements. It may be, for example, that the atoms of the halogens are surrounded by rather complicated fields of force which offer the possibility of being grouped in a variety of stable configurations.

SULFIDES.— K_2S*; FeS trigonal; Sb_2S_3* rhombic; Sb_2S_5; BaS cubic; PbS cubic; SrS cubic; CdS trigonal; CaS cubic; CuS hexagonal; Ag_2S cubic*; HgS_1 cubic, trigonal.

K_2S was found to have a form not previously known. By analogy $(NH_4)_2S$ would be expected to have a new form, but it is not chemically stable enough to allow the trial. An attempt to remove the moisture from Na_2S sufficiently to allow a trial did not succeed.

Ag_2S has been known for a long time to have a second modification above 170°. The transition is accompanied by the evolution of a considerable quantity of heat, as may be shown by taking the cooling curve. There is also a discontinuous change in the electrical resistance on passing through the transition point. No attempt seems to have been made to detect the change of volume, but it has been assumed that in analogy with Cu_2S the change of volume would probably be very small. I made particularly careful search for any evidence of a transition of Ag_2S under pressure. Search was made by the usual methods out to 12000 kgm. at four temperatures, 20°, 120°, 150°, and 200°, and in addition the method of varying temperature from 130° to 200° at approximately 1000 kgm. was used. The change of volume of the transition must certainly be less than 0.0002 cm.^{3} per gm. and it is probably safe to put the limit at a half or a third of this. This experiment answers one question about which there has been some conjecture; it has been thought that at higher pressures the difference of volume of the phases might become appreciable, the transition point at atmospheric pressure corresponding to a maximum or minimum of the transition curve. This experiment shows that the smallness of the difference of volume persists at high pressures; there is no reason to suppose that the transition line will show more than the normal amount of curvature.

Cu_2S is a substance with a transition point at 103°, the character of the transition being very much like that of Ag_2S. The change of volume has in this case, however, been demonstrated to be so small

as to be imperceptible. In view of this known fact it did not seem worth while to make an examination under pressure. The result would in all probability be negative as for Ag_2S.

HgS has two modifications; a very unstable black modification, cubic, and a stable red one. It is known that under pressure the black form changes to the red. I made trial on the red modification over the usual range without result; a negative result is not surprising.

The antimony sulfides have already been extensively commented on, and the other sulfides seem to require no special mention. In the only two cases where the phase diagrams of sulfides have been measured, they have been found to be simple and quite normal in type.

SULFOCYANIDES.— KSCN, II rhombic; NH_4SCN, I rhombic, II monoclinic.

Although the phase diagrams of these two substances differ in appearance, it has been shown in the discussion of individual data that the substances probably are isopolymorphic when modifications in the same crystalline system are put into correspondence. Each substance probably has three modifications instead of two, and the appearance of difference in the phase diagrams is to be explained by the different temperatures of transition.

It is known that RbSCN, CsSCN, and TlSCN also have other modifications. It would be interesting to try them.

HALOGENATES.— $KClO_3$* monoclinic; $KBrO_3$ trigonal; KIO_3 monoclinic; $NaClO_3$ cubic, trigonal, rhombic; $KClO_4$, rhombic.

The relation between the first three potassium salts is not simple. The ordinary form of $KClO_3$ is monoclinic, and that of $KBrO_3$ is trigonal pseudo-cubic. $KBrO_3$ is, however, isodimorphous with $KClO_3$, forming a series of mixed crystals with a gap. It is possible that the ordinary form of $KBrO_3$ is the high pressure form of $KClO_3$. If the usual form of $KClO_3$ corresponds to the second unstable form of $KBrO_3$, the latter might be expected to have three modifications under pressure, but no new one was found. KIO_3 is monoclinic, but will not form mixed crystals with either $KClO_3$ or $KBrO_3$. $NaClO_3$ is cubic, and shows no isomorphism with $KClO_3$. It is known, however, to have two unstable forms, one trigonal and one rhombic, and might on this account be expected to have other forms under pressure.

It would be interesting to try $RbClO_3$ and $CsClO_3$, since these are probably isomorphous with $KClO_3$.

The first one of this group of substances which I investigated was $KClO_3$, my reason was simply that its well known chemical instability seemed to suggest the possibility of readily taking new groupings.

$KClO_4$ is chemically more unstable, however, but shows no new modification under pressure, so the apparent connection between chemical instability and polymorphism turns out after all to have been merely accidental.

In experimenting with members of this group, the danger of explosion has to be particularly guarded against. One very severe explosion resulted from the combination of $NaClO_3$ with the kerosene with which pressure was transmitted. To avoid this possibility, the salts were placed in a nickel steel shell, and pressure transmitted by mercury. There is always the possibility, however, that the shell may split, and the kerosene find its way to the chlorate, as it does for many other substances. In view of this possibility I felt justified in confining my exploration with $NaClO_3$ and $KClO_4$ to only 20°. It remains to this day unexplained why the first three potassium salts did not explode when exposed to direct action of kerosene up to 200° and 12000 kgm.

Organic Compounds.

Halogen Compounds with one Carbon Atom.— CCl_4*, CBr_4*, $CHCl_3$, $CHBr_3$, CHI_3.

The first two of this series have already been discussed. It is unfortunate that CI_4 is too unstable to investigate. The other members of the series are formed by replacing a halogen by an atom of hydrogen. Since this substitution is known to produce important changes in the chemical form, it is perhaps not surprising that polymorphism disappears under the substitution. It is known, however, that lower members of the series, such as CH_2Cl_2 show polymorphism again; the effect of pressure on these substances should be tried.

Benzol and Mono-substitution Products.— C_6H_6*; C_6H_5OH*; C_6H_5Cl; C_6H_5Br; $C_6H_5NO_2$; $C_6H_5NH_2$; $C_6H_5CO_2H$ monoclinic; $C_6H_5NHC_2H_3O$ (acetanilid); acetophenone. It is strange that so few of the crystalline forms are known in this group.

In the comparatively complicated molecules of series like this, one would not expect a substitution for a single atom to have so large an effect on polymorphism as in series of simpler molecules, and it is therefore perhaps surprising that polymorphism is not of more frequent occurrence. But it is to be remembered that the second modification of benzol is stable only at the extreme pressures of the range. It is possibly worthy of remark that the only other member of this series showing polymorphism is the one nearest it in molecular weight.

Because of an accident the exploration with acetanilide at room temperature was made only between 6000 and 12000. At 200°, the approximate coördinates of the melting curve were found to be 6400 kgm. with a change of volume of 0.070 cm.^{3}/gm. The melting point at atmospheric pressure is in the neighborhood of 113°.

Benzol Derivatives with Substitutions for Two Atoms.— Orthokresol*; para nitro-phenol, monoclinic; para toluidine; anethol.

A unique feature of the phase diagram of o-kresol is that the melting curve of I can be realized at *higher* temperatures in the region of II. It is perhaps surprising that p-toluidine does not show another form like o-kresol, since the substituting groups differ so little in molecular weight.

Camphor Group.— Camphor*, trigonal; monobrom-camphor; dibromcamphor; phenylated camphor.

Ordinary camphor has one of the most complicated phase diagrams; it was a surprise that at least monobrom camphor did not have other forms. Monobrom camphor decomposes at about 4000 kgm. at 200° when pressure is released from 12000. Apparently there is no free bromine among the decomposition products. Dibrom camphor at 200° decomposed when pressure had been released from 12000 to 8000 with so large an increase of volume that pressure rose again to 12000. The products of the decomposition were a suffocating gas and much free bromine. There were many indications that neither of these brom camphors began to decompose at 200° until reaching the melting curve. The high pressure as well as the high temperature must play some part in the decomposition, because both of them melt quietly on heating to 200° at atmospheric pressure. Pressure was transmitted to these substances by mercury, so that the kerosene could have had no part in the decomposition.

Runs on phenylated camphor were made at 0°, 20° and 180°. The melting point at atmospheric pressure is −23°; at 180°, 12000 kgm. was not high enough to freeze it.

Compounds of the Type $C\begin{matrix}\nearrow R^1 \\ = O \\ \searrow R_2\end{matrix}$

Carbamide*, tetragonal; Acetic Acid*; Acetamide*, trigonal; Acetone; Formamide; Formic Acid; Oxamide, monoclinic; Propionic Acid.

The first three of these substances form a sub-group very closely

related chemically. They are built up by using the radicals NH_2, CH_3, or OH in various combinations. It is possible, by combining any two of these radicals with $C{=}O$ to build up six compounds. Three of these have polymorphic forms, the fourth, acetone, is liquid throughout most of the range so that new forms would not be expected, the fifth is carbonic acid, $C(=O)(O-H)_2$, which does not exist in a free state, and the sixth, $C(=O)(NH_2)(O-H)$, does not exist. We therefore have polymorphism in all possible cases in this group. The phase diagrams, near the triple point, are similar, in that the transition lines are steep, and the latent heat of transition is small. In closer detail, however, the transition lines are different; those of carbamide and acetic acid are both straight with a positive slope, whereas that of acetamide is distinctly curved and has a negative slope. The diagrams further differ in that carbamide has three modifications and acetic acid and acetamide have only two. We have seen, however, that it is not impossible that acetamide has a third form at lower temperatures, and Tammann [35] says that acetic acid probably has a third form considerably below zero. It may be that the apparent relationship of the phase diagrams is only accidental; what we know about the crystalline forms would suggest this. The system of acetic acid is not known, carbamide is tetragonal, and acetamide is hexagonal. It has turned out of late years, however, that nearly every so-called hexagonal crystal has been found on careful examination to belong to some other system, the apparent hexagonal form being due to the particular manner of twinning. The evidence from the crystalline forms is not conclusive, therefore.

It is worthy of remark that the three radicals forming the compounds just discussed are all of nearly the same molecular weight, OH = 17, NH_2 = 16, and CH_3 = 15. The four other members of the group listed above are formed by using radicals of quite different molecular weight, and in no case were other forms found. Particularly careful search was made in the case of formamide and propionic acid. Two specimens of propionic acid were used, from different sources. Neither was very pure, but the second was somewhat purer than the first.

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35 G. Tammann, Kristallisieren und Schmelzen, p. 277.

The first specimen showed a small discontinuity like a transition in the region of rounding just before melting, which did not appear with the second specimen. Runs were made with this at 0°, 10°, and 21°, pressure being transmitted by mercury. Only at 20° could the pressure be raised to 12000, since at lower temperature the mercury freezes. The approximate coördinates of the melting curve are: 7200 kgm. at 0°, 8100 at 10°, and 9100 at 21°. Two specimens of formamide were also used, both impure. The maximum temperature of examination was 26°. The impurity of the best specimen was considerable, because its melting point was below 0°, whereas that of the pure formamide is listed as +3°. The formic acid used was also very impure, but it showed nothing except a very rounded melting curve at 26° and 50°. If purer materials were easily available, it might pay to try these substances again. My specimens were made especially to order, and are apparently of as great purity as can be produced in an ordinary commercial laboratory.

The oxamide was tried unsuccessfully at 20° and 200°. It decomposed slightly at 200°, as shown by a slight evolution of gas on taking the apparatus apart. Pressure was transmitted directly to the oxamide by kerosene; all the other substances of this group were submerged beneath mercury.

Compounds with two Benzol Rings.— Diphenylamine, monoclinic; Benzophenone, rhombic, monoclinic.

Neither of these had new forms, although benzophenone has several unstable forms.

Substances with Suggestive Mixed Crystal Relations.— $KHSO_4$*, rhombic; NH_4HSO_4*, rhombic; $MgSO_47H_2O$, rhombic; $FeSO_47H_2O$, monoclinic.

The first two of these do not crystallize isomorphously, although belonging to the rhombic system. They form a series of mixed crystals with a gap, the third form being monoclinic. The relations of the several forms have been fully treated in the detailed discussion, and a possible mixed crystal diagram has been indicated. This diagram would demand that the first new form of $KHSO_4$ at high temperatures be monoclinic, and the second new high temperature form rhombic.

The trichromates of K and NH_4 have the same relations as the acid sulfates, and should be tried.

$MgSO_47HO_2$ and $FeSO_47H_2O$ do not crystallize in the same system, but form a series of mixed crystals with a fairly wide gap. If one extrapolates the density of the crystals with preponderating

$FeSO_4 7H_2O$ content to pure $MgSO_4 7H_2O$, a greater density is found than that of the natural form of $MgSO_4 7H_2O$. One is therefore led to expect a second denser form, and to look for it at higher pressures. This matter is discussed in greater detail in Groth's Chemical Crystallography, p. 92. It was a matter of great surprise to me to find that there is no other form at high pressures, for I had regarded this evidence as establishing a greater *à priori* probability for the existence of a new form than for any other substance within my knowledge. Two runs were made on $MgSO_4 7H_2O$. The first was with the pure salt at 20°. For the second run the salt was inoculated with $FeSO_4 7H_2O$. and runs made at 20° and 100°. Higher temperatures were not tried for fear of running into a decomposition of the hydrate. The expected new form should have been found at low temperatures rather than high. Runs were made with $FeSO_4 7H_2O$ at 20° and 100°. At 20° nothing was found out to 12000 kgm., but at 100° a decomposition point of the hydrate was found. This will be described in detail under the group of substances with water of crystallization.

Substances with Water of Crystallization.— Every one of the following list of substances has been investigated both with and without its water of crystallization, except $LiNO_3$, which was tried only in the anhydrous state. For brevity, both the hydrous and the anhydrous salts are specified in the following list only when the crystalline forms are known; in many cases the crystalline form of the anhydrous salt is not known.

Oxalic Acid, $+2H_2O$ — monoclinic, anhydrous — rhombic; Potassium Oxalate, $+H_2O$ — monoclinic; Potassium Acid Oxalate, $+H_2O$*, anhydrous-monoclinic; Potassium Tetroxalate; Potassium Tartrate, $+1/2H_2O$ — monoclinic; Ammonium Potassium Phosphate, $(NH_4)_2KPO_4$*, $+4H_2O$; $FeSO_4 7H_2O$ — monoclinic; $MgSO_4 7H_2O$ — rhombic; $CuSO_4 5H_2O$ — triclinic; $Hg_2(NO_3)_2 2H_2O$*; $LiNO_3 3H_2O$.

All of these substances were tested at the two temperatures 20° and 100°, instead of at 20° and 200°, as for most other substances. All of them were hammered into an open steel shell and pressure transmitted directly by kerosene. With one exception, the water of crystallization was removed by heating to 100° in vacuum for several hours. Potassium Tartrate was dehydrated in vacuum at 160°, since 100° was not high enough.

It is a curious freak of chance that the first substance with water of crystallization that I tried, $Hg_2(NO_3)_2$, showed a transition in the hydrous condition, but not when anhydrous. I was prepared to expect a number of such cases, but the tetroxalate and $FeSO_4 7H_2O$ were the

only others. $(NH_4)_2KPO_4$ has a transition when anhydrous, but not when hydrous. It is to be remembered, however, that only one of these substances belongs to the class whose hydrates have a transition point at atmospheric pressure. The investigation of other substances with known transition points of the hydrates offers a field of considerable interest, but the phenomena are more complicated than those of the simple polymorphic transitions considered here.

The phenomena with $FeSO_47H_2O$ are as follows. It showed two transition points. At 10,000 kgm. there is a transition with fairly large decrease of volume somewhere near 80°; that is, this transition is of the ice type. At 85° there is no transition between 10,000 and 2000, but on cooling at 2000 there is a much smaller reverse transition near 35°. This point is doubtless connected with the known dehydration points at atmospheric pressure, and the other point at 10,000 is probably of the same nature, rather than a true polymorphic transition. It is evident that the dehydration diagram of this substance must be rather complicated. I made no further attempt to study it; there are several serious difficulties in the way of a complete investigation.

Double Salts.— $(NH_4)_2KPO_4$, anhydrous,* and with $4H_2O$; $KNH_4SO_42H_2O$; $ZnK_2(SO_4)_26H_2O$, anhydrous* and with $6H_2O$.

All of these runs were made at 20° and 100°, except $K_2Zn(SO_4)_2$. The first substance has been described under the last heading, and $K_2Zn(SO_4)_2$ has been described in a separate section. It is likely that both of these transitions are really decompositions to the simple salts, rather than a true polymorphic change.

An attempt to make $KNH_4SO_42H_2O$ anhydrous by heating for a number of hours at 150° in vacuum was without success.

Substances with Unstable Forms.— Benzophenone, has four modifications including a monoclinic and a rhombic form; Para-nitro phenol; Acetamide*, trigonal; Menthol; Acetophenone; Monochloracetic Acid, has several unstable forms; Propionic Acid; SbI_3, trigonal; Sulfur*, has a stable rhombic and monoclinic form, and numerous unstable forms; Phosphorus,* cubic, trigonal; Antimony, trigonal; Selenium, two monoclinic and a trigonal form; Arsenic, cubic, trigonal; Iodine, rhombic, monoclinic.

The first seven of these substances have already been commented on, either in this or in earlier papers; the melting curves of several of them have been determined. Phosphorus [B] has been made the subject of a special paper. Antimony, besides being very near phosphorus in the periodic table, forms a number of stable and unstable

modifications at low temperatures. It was somewhat of a surprise that there were no new forms under pressure.

Sulfur is known to have a number of modifications, both stable and unstable, several of them more or less obscure in character, but there are at least two well defined forms that stand to one another in the relation of enantiotropy. I found no other well defined forms to 12000 at 20°, 100°, or 200°. It is possible, however, that a small percentage of the form insoluble in CS_2 was formed by pressure, because the specimen which had been subjected to pressure was not completely soluble. One might possibly expect a new modification of sulfur by an irreversible transition, like that of black phosphorus, because of the proximity of the two elements in the periodic table. On one occasion a piece of sulfur was kept at 12500 kgm. and 200° for six hours, but with no permanent change.

The runs on selenium were started with the amorphous variety, which had been fused immediately before the experiment. It showed no transition to 12000 at room temperature. Pressure was maintained on the amorphous selenium at 7000 for 16 hours with no effect. At 7000 kgm. the selenium was then heated to 200°. There was a transition with decrease of volume somewhere between 20° and 200°, which was doubtless due to the formation of the crystalline phase. At 200°, the new phase showed no transition to 12000 kgm., and also showed none between atmospheric pressure and 12000 after cooling again to room temperature. On releasing pressure the selenium was found to have a density of 4.69. The density of the metallic modification of Se is given as 4.79, and that of the amorphous as 4.29 by Saunders.[36] (It may be mentioned incidentally that several wildly inaccurate values for the density have found their way into some Tables. The Chemiker Kakendar, for instance, gives the density of the amorphous variety as 5.68, and that of the crystalline form as 6.5). There seems little reason to doubt that the substance formed above was metallic selenium, the somewhat small density might easily be due to fissures or occluded kerosene. It is known that ordinary amorphous selenium will crystallize slowly at atmospheric pressure at 200°; the effect of high pressures seems, therefore, to be to lower somewhat the temperature of crystallization. This is as one would expect. Before trying the experiment it seemed plausible to me to expect a new form stable at atmospheric pressure analogous to black phosphorus, because of the similar position of these two elements in the periodic table.

36 A. P. Saunders, Jour. Phys. Chem., **4**, 491 (1900).

Arsenic, again, is near phosphorus in the periodic table, and I thought that there might be another form like black phosphorus, but none was found. The substance used was distilled arsenic; pressure was transmitted to it by mercury, so as to avoid the possibility of poisonous compounds with the kerosene. After the run, the surface of the arsenic was found wet with mercury, and the appearance was that of amalgamation. The mouth of the steel shell was also amalgamated, a thing which I have never observed before under similar conditions of pressure and temperature.

Iodine was tried at 30° and 200° to 12000 kgm. without result. At 200° a much rounded melting point was found near 5000. Because of the great chemical activity of Iodine it was placed in a steel shell beneath water, instead of being allowed to come in contact with kerosene or mercury, as usual. In this way chemical action was largely reduced, but at 200° the Iodine apparently goes slowly into solution.

Substances existing as Minerals in two Forms.— $Pb(NO_3)_2$; HgS, trigonal, cubic; $CaCO_3$, rhombic, trigonal.

$Pb(NO_3)_2$ is said by Morel [37] to have two mineral forms. HgS crystallizes in a black and a red form; the black is very unstable. Both of these substances have been commented on in previous sections.

The $CaCO_3$ was investigated in the form of calcite. In nature $CaCO_3$ occurs in two forms, as calcite and arragonite, the latter being the more dense. There has been considerable speculation as to the relation of these two forms, but it seems to have been finally settled that at ordinary temperatures calcite is the stable form, the reversible transition from calcite to arragonite running at fairly high temperatures. This means that the phase diagram must be of the ice type. There is, therefore, a possibility that a permanent change from calcite to arragonite might be brought about by increase of pressure, if the pressure could be carried far enough into the region of stability of the arragonite to force the reaction from calcite to run, and the pressure then released in a region where the reverse transition from arragonite to calcite does not run because of viscosity. The experiment was tried of maintaining pressure on calcite at 12500 kgm. for six hours at 200°, cooling it, and then releasing pressure, but there was no permanent change of density. Since the reaction from arragonite to calcite does not run at atmospheric pressure and room temperature, it would run

[37] J. Morel, Bull. Soc. Min. France, **13**, 337 (1890).

still less at higher pressures at room temperature. Therefore, if arragonite had been formed at all in this experiment, the reverse transition would not have run, and we infer that 12500 kgm. at 200°, is not a high enough pressure to bring the calcite into a region where the reaction to arragonite spontaneously runs. The specimen used was not large enough to enable me to tell whether there was any reversible change in the calcite itself up to 12000 at 200°.

Substances with Reversible Transitions at higher Temperatures.— K_2CrO_4, rhombic, triclinic; K_2CrO_7, two triclinic forms; Cu_2I_2*, cubic.

These all have transitions near a red heat; it is not known to what type they belong. If they were of the ice type, a high pressure might bring the transition down to the range of this work. Reason has been given for supposing that the transition found at 200° for Cu_2I_2 is not the same as the previously known high temperature transition.

Organic Acids.— Carbolic*; Acetic*; Monochloracetic; Stearic; Tartaric, monoclinic; Benzoic, monoclinic; Oxalic, rhombic; Citric; Propionic; Formic.

Pressure was transmitted to all of these substances by mercury.

I have already mentioned we would expect from Tammann's theory of polymorphism that enantiotropic transitions would be particularly common among the organic acids. Out of ten substances tried, only two examples were found, and these were not new examples, but were known before. If ten is a sufficient number of instances to give the law of chances a fair test, this is not favorable to the theory.

In the above list, monochloracetic acid, which has been previously mentioned, has unstable forms, but this sort of transition is not contemplated by Tammann's theory. Oxalic acid has also been mentioned; it was tried with and without the water of crystallization. Citric acid is listed as crystallizing with water, but as I could produce no change in its appearance by heating to 100° in vacuum for several hours, I assumed that it had been supplied in the anhydrous condition.

The tartaric acid was dried in vacuum at 100°. At 12000 kgm. it showed no change on heating from room temperature to 200°, but on releasing pressure at 200°, decomposition began at 5000 with an increase of volume large enough to bring the pressure back to at least 7100. The product of decomposition was a sticky putty-like mass, which swelled up and overflowed the mouth of the tube when the apparatus was opened after cooling. The Nickel steel shell was split. Professor Kohler was kind enough to examine the substance, and found that it was one of the anhydrides of tartaric acid.

ELEMENTS: Hg, cubic; K, tetragonal; Na, tetragonal; Sn*, rhombic, tetragonal; Bi, trigonal; Tl*; S*, rhombic, monoclinic; P*, cubic; I*, rhombic, monoclinic; As*, cubic, trigonal; Sb*, trigonal; Se*, monoclinic (2), trigonal.

The investigation of mercury was concerned primarily with the melting curve. Its freezing behavior is known to be abnormal, but since the freezing temperature is a much smaller fraction of the critical temperature than it is for most other substances, one would not perhaps expect the abnormality to result in polymorphism. Sodium and Potassium show nothing unusual. Perhaps, from the rather rapid approach of Δv toward zero, Potassium might be regarded as a candidate for polymorphism at some pressure beyond the range of this work. Bismuth would be expected to have another form because its melting is of the ice type; it is a great surprise that it does not. Thallium has another known form; the change of volume is so small that I could not make accurate measurements.

The reason for trying Tin was that it is known to have a transition point at 20°, with a large change of volume, the low temperature phase (gray tin) being the less dense. A phase diagram like that of AgI might be expected. The transition from white to gray tin is known to be enormously viscous, so that one could not expect to observe this, but there was a possibility that the reaction to Tin III, if there is such, might run more readily. No such transition was found. It would be of interest to start with pure gray tin, and subject this to pressure at a low temperature.

Werner [38] has recently given a provisional location for a transition line between two varieties of white tin. The transition point at atmospheric pressure is at about 160°, and at 200°, it is 500 kgm. The change of volume is extraordinarily small, so small that I could hardly expect to detect it with my apparatus at a pressure so low as 500 kgm., where it is most insensitive.

The other elements have been described in a previous section.

MISCELLANEOUS SUBSTANCES.— H_2O*, trigonal; CO_2; KNO_2*; $K_4P_2O_7$; $K_4S_2O_7$; K_2CO_3; $KHCO_3$, monoclinic; Potassium Acid Tartrate, rhombic; Methyl Oxalate, monoclinic; Urethane*; Naphthaline, monoclinic; Cane Sugar, monoclinic.

H_2O has a phase diagram exceeded in number of phases only by NH_4NO_3, and possibly by camphor. CO_2 was at first thought by Tammann, to have a triple point with the liquid near 4000, but he

[38] M. Werner, ZS. Anorg. Chem., **83**, 275 (1913).

later withdrew this. I could find none to 12000. KNO_2 shows a transition line of rather large and unusual curvature; it is unfortunate that the substance was so impure.

The reason for trying the six substances from KNO_2 to Potassium Acid Tartrate was merely that polymorphism seemed to be rather more common among the compounds of Potassium than of other elements, and it seemed worth while to try a number of examples. If this surmise is correct, these six substances were not such as to bear it out. $K_4P_2O_7$ was tried only at 20°, because it had some water in it. $K_4S_2O_7$ was tried at 20° and 200° as usual. Both were without result. Several runs were made with K_2CO_3. The first showed a small transition near 6500 kgm. at 200° and at a somewhat higher pressure at 185°. This was found unmistakably with two different fillings of the apparatus. But after standing in the apparatus for three days, the transition at 185° had entirely disappeared, and that at 200° had a smaller change of volume. An attempt to repeat the measurements after six months showed no trace of the transition. The result is hard to explain. I am inclined to think that the transition may be a genuine one, but that 200° is in the very viscous region, so that sometimes the transition will run, and sometimes not. The effect may, however, be due to moisture; the first specimen may possibly have been a trifle moist, but the second was carefully dried in vacuum.

Methyl Oxalate was tried because Tammann [39] has announced two modifications. I could find no other form; the matter has been discussed at considerable length in the paper on melting.

There was no particular reason for trying Urethane, except possibly its rather interesting method of decomposition on heating, and its polymorphism seems to have no suggestive connection with that of other substances. Naphthaline and Sugar offered no special promise of polymorphism; they are simply substances readily available for miscellaneous exploration.

Discussion.

A compact summary of the nature of the effects for all the polymorphic transitions investigated to date is given in Figures 30 and 31. These diagrams show the location of the transition lines between the several phases, which are indicated by Roman numerals or by L for the liquid; the arrows on the lines show the direction in which Δv

[39] G. Tammann, Kristallisieren und Schmelzen, p. 265.

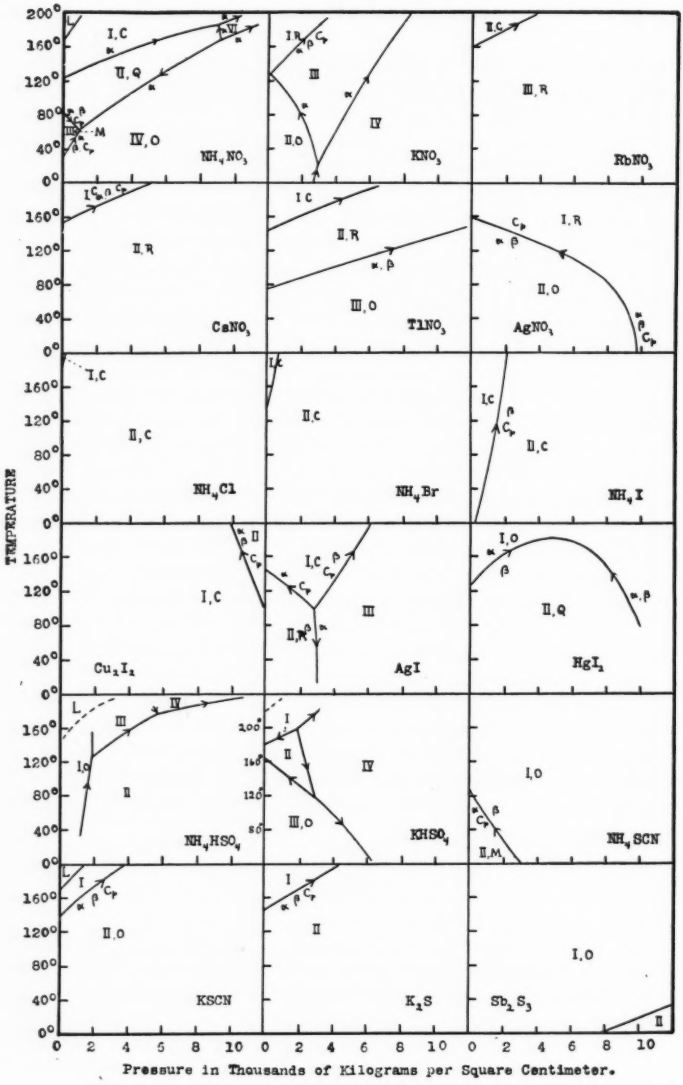

FIGURE 30. Collection of Results.

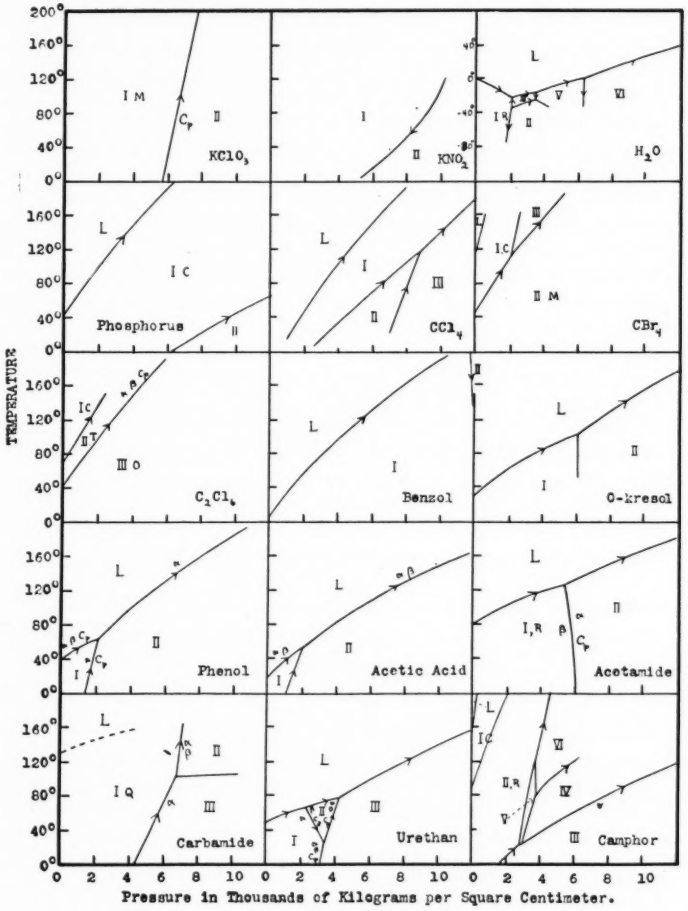

FIGURE 31. Collection of Results.

decreases numerically, an α, β, or C_p to one side of the line indicates that on that side of the line the compressibility or the thermal expansion or the specific heat is the greater, and the crystalline systems have been indicated in those cases where known by letters. The abbreviations used for the crystalline forms are: C, cubic; Q, tetragonal or quadratic; R, rhombohedric or trigonal, including hexagonal; O, orthorhombic, or rhombic; M, monoclinic; T, triclinic.

The diagrams bring out the fact, which was also brought out by the general survey, that mere chemical similarity is not sufficient to ensure similarity of phase diagram. A polymorphic change cannot be regarded, except from certain restricted thermodynamic view points, as a special case of a chemical reaction, but involves different and undoubtedly more mechanism. Similarity of the phase diagram of two substances involves a much more far-reaching correspondence of mechanism than similarity of chemical behavior. There are, as a matter of fact, only two groups of phase diagrams in the collection above which are equivalent. They are $RbNO_3$, $CsNO_3$, $TlNO_3$, with a remote possibility of KNO_3 on the one hand, and NH_4Cl, NH_4Br, NH_4I on the other. In these cases it seems to be a first prerequisite for similar phase diagrams that the corresponding phases form complete series of mixed crystals in the range of temperature in which corresponding modifications of both pure components are stable. It would seem, however, that thorough going correspondence of phase diagrams demands a higher order of identity than simply ability to form a continuous series of mixed crystals at some one temperature and pressure. A probable example of this is $KHSO_4$ and NH_4HSO_4. It is very likely, although not definitely proved, that the ordinary rhombic form of NH_4HSO_4 is identical with the form of $KHSO_4$ above 180°, and that at pressures and temperatures in the region of stability of $KHSO_4$(I) the two salts form a continuous series of mixed crystals, unless indeed it should chance that one of the melting points is too low. On the other hand, it is conceivable that two substances should have corresponding phases with corresponding diagrams, but, because of special relations of the transition temperatures, no region of continuous mixed crystals. For instance, if the entire phase diagram of $TlNO_3$ were lifted to higher temperatures so that the transition from trigonal to rhombic takes place at say 160°, there would be no region in which the trigonal forms of $CsNO_3$ and $TlNO_3$ are completely miscible, but nevertheless the two phase diagrams would be closely corresponding. Whether cases of such large displacements of corresponding transition points occur in nature is a matter for experiment.

It is evidently useless to try to generalize from only the two groups found here. This conclusion does seem justified, however; similarity of phase diagrams between corresponding phases is evidence of identity of structure of a higher order than is concerned in the ordinary run of chemical or crystallographical phenomena. In general, the identity of structure must be complete enough to allow continuous series of mixed crystals, but this identity is not necessarily far reaching enough. Instances of such far reaching identity must be rare; it is all the more important to investigate other cases.

Similarity of phase diagrams means not only an identity of structure so complete that similarly arranged edifices are possible, but also means that the fields of force surrounding the elements are so similar that corresponding edifices are *stable*. This has a bearing on the custom of many crystallographers of classifying a substance as dimorphic if it can crystallize in limited proportions with another substance of different symmetry. Such a "dimorphism" cannot be of broad significance; it merely means that the similarity of the building stones of the two substances is great enough so that if sufficient compulsion is applied to the one set they may combine in limited proportions in the edifice appropriate to the other. A very wide range of similarity or dissimilarity is evidently included in a classification so elastic as this.

It is also the custom, or rather a matter of definition, to class a substance as polymorphic if it has more than one modification, stable or not. This again, has no well defined significance. Given a number of identical building blocks, it would evidently be possible to build these with our hands into a large variety of assemblages corresponding to different crystalline systems. Most of these arrangements would be very unstable, but all would persist for a small interval of time. This means that in this sense every substance is polymorphic in a very complicated way. In practise, however, not very many substances under ordinary conditions happen to form assemblages that are comparatively stable. But it is conceivable, and likely, that under different conditions of inoculation or subcooling the number of substances with unstable polymorphic forms (monotropic polymorphy) should be very largely increased. The point is that this kind of polymorphism is not of absolute significance, and the more we extend the list of polymorphic substances by increased skill in manipulation, the less significant does it become. There is no denying, of course, that the easy and persistent polymorphism shown by phosphorus, for example, is significant — it is merely impossible to draw a sharp line. Further-

more, many cases now classified as monotropically polymorphic would turn out to have larger significance if certain lines of conjecture prove to be justifiable. Many investigators have thought that forms unstable under atmospheric conditions would become stable at higher pressures. In this case such substances would become as significant as those enantiotropically polymorphic under ordinary conditions.

The experiments above have shown, however, that in none of the cases examined have forms ordinarily unstable become stable at higher pressures. This is, after all, not surprising, because the majority of unstable forms are less dense than the stable forms. Their region of stability, if it exists, is at negative pressures. The example of $MgSO_4 7H_2O$, mentioned above, is a case on the other hand where the unstable form is more dense, but is not formed at high pressures, even when inoculated. The dense unstable form of $MgSO_4 7H_2O$ may be obtained in the pure state by crystallizing from the supersaturated solution on inoculation with a crystal of $FeSO_4 7H_2O$.

Cases have been found, however, in which a phase unstable at high pressures becomes stable at relatively higher pressures. Water below 0° and near 6000 kgm. crystallizes most readily in the form of ice VI, which is unstable, in preference to the stable form, ice V. Ice VI is the denser form and becomes stable at higher pressures. Acetamide is another similar example. The case of o-kresol is of the opposite kind. Above the triple point the unstable modification I is very much more likely to crystallize from the melt than the stable form II. I is the less dense form, and it has a domain of stability at lower pressures, corresponding to negative pressures for ordinary substances. Although there are these examples showing the possibility in some cases of an unstable modification acquiring a region of stability, it is likely that in the majority of cases the unstable forms have no region of stability within experimental reach.

It seems preferable on the whole, therefore, in this discussion to confine the use of the word polymorphic to those substances with two or more phases which are capable of reversible transitions. It is of interest to inquire what is the frequency of occurrence of polymorphism. I have already emphasized that an examination like that above of many substances cannot possibly disclose all cases of polymorphism; a number of stable forms will not appear because of viscous resistance. The phase diagrams afford several cases where the new phase would not have been discovered if the exploration had been confined to the low temperatures. Examples are $KHSO_4$, HgI_2, and o-kresol. It is not possible to give any general rule that will show

in what region a transition will become so viscous that it cannot be observed, because the behavior of different substances is very different. As a general rule, however, the viscous resistance to transition becomes greater at greater distances from the liquid phase. Substances with high melting points would be expected to show less frequent polymorphism. Now in all the above list of substances with polymorphic forms, the highest melting point is 628°. Not one of the substances examined which has a higher melting point shows polymorphism in my range. The only example among substances which I did not examine is Cu_2S with a melting point of 1100°. There are, however, numerous examples known of polymorphism at higher temperatures; several of the substances examined above belong here. It is therefore likely that many of the substances would show polymorphism if examined over a wider range. It is, furthermore, significant that the nitrates, among which polymorphism is widely prevalent, are all low melting, as are also the iodides. The organic compounds all have low melting points; in the above list there are 39 organic compounds, of which 11 are polymorphic. This does not include substances with unstable forms. Of the inorganic substances with known melting points below 650°, 25 out of 42 are polymorphic. Polymorphism seems of more frequent occurrence with inorganic compounds. As a general average, perhaps one out of three substances are polymorphic.

We next examine the relative frequency of occurrence of the different crystalline systems. I have not yet been able to determine the system of any of the new forms stable at higher pressures; we cannot yet tell whether all substances tend to any one simple type under high pressures. The known forms include 17 cubic, 3 (or 4) tetragonal, 8 trigonal, 11 rhombic, 4 monoclinic, and 1 triclinic. The relatively high frequency of the rhombic system is perhaps surprising. The number of cases in which the cubic form, which has the highest symmetry, is of greater volume than a neighboring more unsymmetrical form is striking. It would perhaps be natural to expect that the forms stable at the higher temperatures, with the greater energy of temperature agitation, and in many cases the greater volume, would have fewer elements of symmetry. However, in 10 of the above 17 cases, the cubic crystal may be transformed by proper change of pressure and temperature to a phase of smaller volume and also of lower symmetry. It is evident that the cubic arrangement in these cases cannot be the arrangement of closest packing. There is, of course, no especial reason to expect it when the crystal is built up of different kinds of atoms. Out of the five cases above in which a trigonal form

adjoins a known form, four are cases in which the trigonal form adjoins another either of smaller volume and lower symmetry, or larger volume and higher symmetry. The general rule seems to be the reverse of what we would expect, the phase of higher symmetry in the majority of cases has the larger volume.

In this connection it is also interesting to note that there are several cases in which the same crystalline system occurs in more than one phase of the same substance. NH_4NO_3 has two tetragonal forms (possibly these are identical), $RbNO_3$ has two trigonal forms, probably $KHSO_4$ two rhombic, and of course NH_4I, NH_4Br, and NH_4Cl are a striking series in which the different modifications belong to the same sub-group. This shows that there is no restriction placed on the total number of possible polymorphic forms of any one substance by considerations of this character. As far as this goes, we might have more than 32 modifications.

It would seem that in our present state of knowledge the specification of the crystalline system of different polymorphs is without special significance, but is of value chiefly as a means of identification. And probably when we are able to give a more detailed description of the structure, specification of the crystalline system will be superfluous.

We now turn from crystallographical considerations, and discuss the general thermodynamic aspects of the phase diagrams. The enormous complexity of the phase diagrams of solids as contrasted with the melting diagrams is apparent. There are only two known melting curves that fall in temperature with rising pressure, those of water and bismuth; all others rise. The rising melting curves rise indefinitely, with no suggestion of a maximum or a critical point. All the melting curves, whether rising or falling, are concave toward the pressure axis. On every one of the curves Δv decreases with rising temperature, and on every curve where accurate enough measurements can be made, the curve plotting Δv against pressure is convex toward the pressure axis. Furthermore, the liquid is universally more compressible, and of a higher specific heat than the solid, and only one case is known in which the liquid has a smaller thermal expansion, that of water over a restricted range.

None of these uniformities hold for polymorphic changes. Retrogressive transition lines are of fairly common occurrence. Wallerant makes the statement in his Cristallographie that there are only four known transitions of this type; AgI, NH_4NO_3, Boracite, and Calcium Chloraluminate. In all, sixteen such transitions have been examined above, fourteen of them not known to Wallerant. It appears, then,

that nearly one quarter of all the transition curves are of the ice type. The persistence of the curves for $AgNO_3$ and HgI_2 suggests that an ice type of transition may be as capable of continued stability over a wide range of pressure and temperature as an ordinary transition. In the early stages of this work I was inclined to regard the existence of an ice type of transition as *à priori* evidence that there must be at higher pressures a normal transition to supplant it, as on the melting curve of ice I. This surmise did not prove fruitful.

A summary of all the transition lines examined is shown in Table XIV. This shows the number of various classes of lines grouped according to important characteristics. Thus, for example, out of 69 lines examined, there are 3 rising curves whose direction of curvature is abnormal, and whose direction of variation of Δv is also abnormal. In drawing up this table, normal behavior has been called that which is like that on the melting curve. In detail, normal curvature is concavity downward, normal variation of Δv is decrease with rising temperature, α and β are normal if the phase of larger volume is the more compressible or expansible, and C_p is normal if the phase stable at the higher temperature has the higher specific heat. In drawing up the table all those lines which are sensibly straight, 33 out of 69, were not tabulated as of either normal or abnormal curvature, but their other properties were tabulated under the normal branch. The results for HgI_2 have not been included at all, because its curve both rises and falls.

In general the normal type of behavior preponderates, but the possibilities that have been discovered are so numerous that one would be prepared to admit that after extensive search probably representatives of every one of the divisions could be found. It is certainly evident that the mechanism of polymorphic transitions in different substances does not possess any one notable characteristic which expresses itself in a common type of behavior on all the transition lines, as is the case for melting.

Two significant features of the table call for comment. In the first place, abnormal curvature means that the factor by which the change of volume is multiplied to give the change of internal energy becomes smaller at higher pressures. This factor is called by some writers the internal pressure, and is taken as a measure of the internal cohesion. It is at first surprising that this cohesion should become less as the substance is compressed so as to occupy less volume. It is difficult to imagine the possibility of such an effect in a substance composed of spherical molecules. The effect must be due to the configu-

ration of the molecules and the location of the centers of force — when the new modification is formed the centers of force are torn farther apart, but the geometrical centers come closer together. In the second place, the number of cases in which the compressibility is abnormal cannot but be significant; there are 17 abnormal cases against 10

TABLE XIV.

SUMMARY OF BEHAVIOR OF TRANSITION LINES.

					α	β	C_p
Rising	53	Normal	34	N.	8	4	4
				Ab.	7	4	5
		Curvature	18				
				N.			
			4				
				Ab.	1		
		Abnormal	4	N.		1	1
				Ab.	2	2	2
		Curvature	9				
				N.			
			3				
				Ab.			
Falling	16	Normal	6	N.			3
				Ab.	4	1	
		Curvature	8				
				N.	1	2	3
			8				
				Ab.	3	2	
		Abnormal	1	N.	1		
				Ab.		1	1
		Curvature	1				
				N.			
				Ab.			

normal cases. As a rule, therefore, the phase of larger volume is the less compressible. A possible way of understanding this is described later.

In connection with the multiplicity of type of transition lines Roozeboom's classification of triple points may be mentioned. He recognized eight different varieties, according to the relative location of the lines in different quadrants. Figure 32 shows the groups. At the time that he wrote examples of only one group were known, his group 4. The data above include examples of groups 1, 2, 3, 6, and 7. The only cases now missing are 5 and 8. The number of cases in the respective groups are 1, 1; 2, 4; 3, 5; 4, 8; 6, 2; and 7, 1.

Although the transition lines present great complexity of shape, there are two special types of which no examples have been found, lines with a minimum temperature or a critical point. The minimum temperature does not seem essentially different from a maximum, and

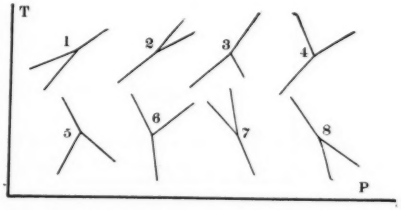

FIGURE 32. Reproduction of Roozeboom's classification of triple points.

there is no reason to suspect that such cases may not exist. But it is different with a critical point. If such exists, it means that by going around this point we can pass by continual gradations from one crystalline system to another. Whether such a possibility exists is open to grave question. It is at least significant that no case of it has been found above. The closest approach to it was on the IV–VI line of camphor, which could not be studied much further because of the extreme stickiness of the transition. Perhaps theoretically there is no objection to such a transition; we can imagine for instance that after a certain stage in the uniform compression of a cubic lattice one of the dimensions begins to change differently from the others, and the crystal becomes tetragonal. But although we can imagine the kinetics of such a change of system, we cannot conceive any adequate physical reason for such a change, and it is certain that any such change of system would be fundamentally opposed to all our present experi-

ence of crystals. It is easy to prove that if Neumann's law holds, that is, if all the other physical properties possess all the elements of symmetry of the crystalline form, then a uniform hydrostatic pressure or a uniform change of temperature cannot so change the dimensions of the crystal as to alter its crystalline system. The existence of a critical point is not compatible with Neumann's law. If Neumann's law expresses some fundamental fact of crystal structure, as it probably does, then we are morally certain that a critical point does not exist, and if a critical point should be discovered, this alone would be sufficient to dethrone Neumann's law from a position of vitally fundamental importance.

There is another possibility. Instead of suddenly stopping at a critical point, where the volumes of the two phases become equal, the transition line might suddenly stop at a point where the volumes were different, and spread out into a fan shaped region occupied by a con-

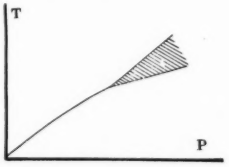

FIGURE 33. Showing a conceivable degeneration of a transition line into a region of mixed crystals.

tinuous series of mixed crystals of the two phases as shown in Figure 33. But although this sort of thing is possible thermodynamically, such a phenomenon would be even more foreign to our experience than a critical point, and in all probability does not exist. Such an effect would be detected experimentally by a continuous change of volume throughout the shaded region. Never in any of my work have I found anything to suggest such an effect.

It is interesting to inquire whether the theory of solids derived from quantum hypothesis has any restrictions to impose on the shape of the transition lines. The quantum hypothesis when applied to solids demands that in the neighborhood of the absolute zero C_v and the thermal expansion are proportional to the third power of the temperature, and that the compressibility is constant. That is, $\left(\frac{\partial v}{\partial p}\right)_\tau = \alpha$, $\left(\frac{\partial v}{\partial \tau}\right)_p = \beta\tau^3$, and $C_v = \gamma\tau^3$, where α, β, and γ are con-

stants. An easy thermodynamic transformation gives the relation $C_p = \gamma\tau^3 - \frac{\beta^2}{a}\tau^7$. Now if we assume that each phase separately satisfies these conditions, except with different values of the constants, and if we write down the condition of equality of the thermodynamic potentials of the two phases, we shall find for the equation of the transition line near the absolute zero,

$$ap^2 + bp\tau^4 + c\tau^8 + dp + e\tau^4 + f = 0,$$

a conic in p and τ^4, where,

$$a = \frac{\alpha_1 - \alpha_2}{2}, \; b = \frac{\beta_1 - \beta_2}{4}, \; c = \frac{1}{56}\left[\frac{\beta_1^2}{\alpha_1} - \frac{\beta_2^2}{\alpha_2}\right], \; d = v_1 - v_2,$$

$$e = -\frac{\gamma_1 - \gamma^2}{12},$$

$$f = E_1 - E_2.$$

E_1 and E_2 are the internal energies of the two phases at 0° *abs.* and zero pressure.

It may be shown immediately by differentiation that the curve approaches the pressure axis perpendicularly, a fact which, of course, has been known for some time. It is easy to see by solving the equation for p at $\tau = 0$, that the following conditions must hold if there is a transition at absolute zero at some positive pressure. The existence of such a transition point is compatible with either a positive or a negative value for a. If the phase of larger volume is more compressible, no restriction is placed thereby on b, and no restriction placed on $E_1 - E_2$ $(= f)$ as to sign, but there is a restriction as to magnitude to insure that p shall be real. If the phase of larger volume is less compressible, no restriction is thereby placed on b, but $E_1 - E_2$ must be negative and not too large. That is, the internal energy of the phase of smaller volume must be greater in this case. Whether the transition line, which is vertical at the axis, bends to the right or the left at higher temperatures depends on the sign of b; it curves toward the temperature axis if the phase of larger volume becomes more expansible at higher temperatures, and conversely.

The only result of this analysis of immediate interest is that quantum hypothesis still leaves open the possibility of various types of behavior at absolute zero, and in so far does not demand phenomena different in kind from those which we have found within our range.

There is another interesting point in connection with polymorphic transitions at the absolute zero. If at the absolute zero a transition runs irreversibly, in the metastable region, it is accompanied by evolution of heat, according to the equation $\Delta H = (v_1 - v_2)\Delta p$. This is demanded by the law of the conservation of energy. The idea of heat in finite quantities playing any essential or necessary part in phenomena at absolute zero seems at first a little strange. It means that in the mechanism of polymorphism there is something that during the change converts potential into kinetic energy.

At higher temperatures there is an interesting suggestion for the quantum theory of solids in the fact that there are polymorphic phases which are stable at the higher temperature, but have the lower specific heat. That is, the modification of higher specific heat absorbs heat and passes to a modification of lower specific heat. If the total heat (kinetic energy) content of either modification is equal to the heat absorbed in warming from absolute zero ($= \int c_p d_\tau$) then certainly the specific heat curves of the two modifications cannot be of the same character all the way down to the absolute zero, but one must cross the other. Therefore the expression for the energy of the two phases cannot be of a universal type, differing only by the numerical value of a characteristic constant, as are the ordinary expressions of quantum theory. This means that substances with polymorphs cannot be treated like monatomic crystals, which is not surprising; but it also means that the characteristic function of more complicated salts is a function not only of the kinds of atoms, but also of their arrangement. Of course we have applied considerations above to C_p which properly apply only to C_v, but this can usually be done without sensible error.

It is interesting to note in this connection that from the values which we have given above for $\Delta\alpha$, $\Delta\beta$, and ΔC_p, we cannot calculate the value of ΔC_v. ΔC_v cannot be obtained from the equation of the transition line and the difference of compressibility or C_p; to calculate it we must know the absolute value of at least either the compressibility, expansion, or C_p.

The last part of this discussion is to be occupied with considerations intended to make understandable how it is that there are polymorphic changes, and that the phenomena are as complicated as we find them. This will not be a theory of polymorphism in the proper sense of the word.

Brief mention should be first made of the recent theory of polymorphism of Smits[40]. His theory is that any substance which shows

40 A. Smits, Proc. Amst. Acad., numerous papers (1910–1915).

polymorphism forms at least two different kinds of molecules, and that these two kinds of molecules are present in both phases, but in different proportions. Furthermore, the ratio between the two kinds of molecules in a single phase varies continuously with temperature. It must be frankly recognized that this theory has succeeded in correlating a formidable array of chemical facts, many of them new, but nevertheless it seems to me that the picture it presents of the mechanism of a crystal involves considerable physical difficulties. It is hard to see how components of varying proportion can be arranged on definite space lattices, as we know they are. The modern conception of the crystal is one for which the molecule has lost its significance. We know that when we build up a crystal from its elements out of solution or the melt, these elements are added as entire molecules; or when a crystal is taken apart, as by melting, the crystal comes apart in molecules. Inside the crystal, however, the molecular bonds lose their individuality and fuse together. The molecular bond makes its appearance only when we try to remove a part from the crystal. Certainly as a thermodynamic entity, concerned with specific heats, the molecule has little significance for crystals.

It is significant that none of Smits' results were obtained with single crystals, but with aggregates of small crystals. Between the crystal grains there must be transition layers more or less amorphous in character, and the idea of association may be applicable within these layers. It is not unreasonable to suppose that the phenomena which Smits finds are consistent with the idea of a varying association are connected with the transition layers. At any rate it seems to me that at present we should withhold acceptance of Smits' theory, in spite of the chemical facts on its side, until he has shown by actual X-ray photographs that in an individual crystal, of HgI_2 for example, there is the continuously varying constitution demanded by his theory.

This discussion is to be guided by the same idea as that underlying a previous discussion of the thermodynamic behavior of liquids under high pressures. It turned out that the experimental facts were of an unexpected complication, a complication so great that previous pictures of the atoms as smooth spheres were powerless to provide a sufficient range of possibilities. It was the purpose of that discussion to show that if we made the next degree of refinement in our representation of the atoms and considered them as having characteristic shapes, that we had thereby opened up at least the possibility of explaining all the effects. The purpose of this discussion is the same; to show that if we go to the next stage of refinement and consider

the effect of the shape of the atoms, we have in our hands at least a possibility of explaining the complicated facts of polymorphism. As a matter of scientific economy, we are bound to push as far as we can the possibilities of the next stage of refinement. The discussion will in part take the form of showing in detail how some of the unexpected effects which we have found may be exhibited by aggregates of building blocks with definite shapes.

The crystal is supposed to be composed of units, atoms or molecules as the case may be, which remain the same in different polymorphic forms. Polymorphism is to be regarded in its most general aspect as due to regrouping of these units in different arrangements. This does not rule out at all the possibility of such special groupings as are considered in the association theories in which larger related groups may be distinguished. Each one of the units is to be thought of as terminated by rigid boundaries, that is, each unit has a shape as definitely as a brick has shape. Furthermore, at different localities on the surface of the units there are localized centers of force (attractive usually) so that two units, if free, will tend to come together with a definite orientation. A crystal is to be regarded as a system in which a compromise has been affected between the arrangement which the units would take in virtue of the action of the localized centers of force, the arrangement into which the units would be urged by the external pressure or the mean internal pressure so as to occupy the smallest possible volume, and the chaotic disarray which temperature agitation tends to produce.

This conception of an atom or molecule as a hunk of matter of definite shape and with localized centers of force is no doubt crude from certain points of view. We require a more detailed picture to account for the scattering of α particles, for example. But it does seem to contain enough of the essentials of the situation to make it a suggestive tool of thought in dealing with polymorphic changes. Doubtless a more valid picture of the atom is as a field of force. But in the last analysis this comes down to much the same thing as saying that the atom has shape. All that we mean when we say that any object of our experience has shape or boundaries is that as we approach the object the force with which it acts on us changes at a certain stage very rapidly into an intense repulsion. Our idea of shape is only a qualitative one, depending on how fast the repulsive force increases. It is worthy of remark that if we regard the atom as essentially a field of force we shall find that in order to account for the observed facts this field of force must become very rapidly a repulsion beyond a

certain critical distance. Thus Grüneisen,[41] who has succeeded in correlating many of the thermodynamic properties of solids by assuming the atoms to be the centers of attractive and repulsive forces uniform in all directions, finds that the repulsive force must vary at least as the inverse twelfth power of the distance, while the attraction varies as the square. So rapid an increase of the repulsive force means a close approach to the phenomena of a definite boundary. As for regarding the atom (or unit) as possessing a definite geometrical shape other than spherical, we cannot well do otherwise, for the very existence of crystals shows that the field of force about an atom is not uniform in every direction. It has perhaps been more usual to regard the crystal unit as a rigid sphere with localized centers of attractive force. But this seems to be an unnecessary and unjustifiable restriction. From the point of view of the field of force, this is equivalent to saying that the attractive forces are unsymmetrically deposed, whereas the repulsive forces are symmetrically directed toward all sides.

The atom or molecule need not be thought of as absolutely rigid. It must of course be deformable to a certain extent, and there is experimental evidence (the increase of energy of a liquid if isothermal compression is carried beyond a certain point[42]) that such an effect is actually of importance. Furthermore, the temperature agitation in a solid is doubtless largely a matter of internal agitation of the molecules, rather than of motion of the molecules as wholes.

One of the puzzles of polymorphic change is offered by substances like benzol, in which the transition has no latent heat, but the internal energy of the phase of smaller volume is the greater. If the forces between the molecules are on the whole attractive, then we should expect the potential energy to be decreased when the molecules are brought closer together, instead of increased. An increase of energy would be expected only if the approach of the molecules took place against an average repulsive force. But if the force is on the average repulsive, it is difficult to see why the molecules become unstable and assume a new arrangement. However, if the atoms have properties like those above, this becomes understandable. Figure 34 shows schematically what may be the arrangement in the phase of larger volume. The molecules assume such an arrangement that the localized centers of force approach as closely as possible. This is the

41 E. Grüneisen, Ann. d. Phys., **39**, 257 (1912).
42 G, p. 95.

arrangement of minimum potential energy. But this is not the arrangement of smallest possible volume. As pressure is increased the molecules may be forced to turn into the positions of Figure 35, occupying the minimum volume. In this arrangement the attractive centers have been torn apart, and the potential energy has been increased.

This point is one of wide importance. If we suppose that the energy of temperature agitation is the same in two different phases at the same temperature, the mere existence of transitions for which there is no latent heat and all the work done by the external pressure is stored up as an *increase* of internal energy, affords conclusive evidence that the forces with which the atoms act on each other cannot be effectively situated at the centers of the atoms. The assumption of

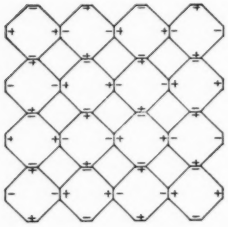

Fig. 34.

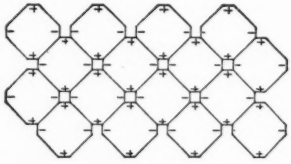

Fig. 35.

FIGURE 34. Hypothetical substance composed of approximately square atoms.

FIGURE 35. The atoms of Figure 34 in another arrangement. The arrangement of largest volume is that of minimum potential energy.

central forces is one that has been very widely used, from the early writings of Poisson on theoretical elasticity to the recent speculations of Grüneisen. These considerations show that this is not an adequate method of representing the inter-atomic forces, at least when the atoms are close together as in a solid. The effective centers of atomic attraction are not situated at the geometrical centers of the atoms, but must be nearer the surface. It is furthermore probable that the centers of attraction are *very* near the surface, because the nearer they are to the surface, the easier it is to conceive, without doing violence to our other conceptions of the atom, how it is that pushing the geometrical centers closer together may pull the centers of attraction further apart.

Another puzzling question is how we are to account for the phase at the higher temperature having the smaller volume. The diagrams above show how this may be. The localized centers of force are situated on projections some distance from the center. At low temperatures, when the energy of agitation is small, the molecules arrange themselves in a form in which the centers of force neutralize each other, producing a crystal with large open framework. But with increased temperature agitation, the forces at the apexes can no longer withstand the disrupting effect, and above a certain temperature the points are shaken loose, and the molecules settle down to the arrangement of smaller volume. Evidently high pressure also tends to produce the phase of smaller volume, so that at high pressure the temperature need not be raised so high to shake the crystal into the phase of smaller volume. In other words, when the volume of the high temperature phase is smaller, increased pressure lowers the transition point.

In the summary of Table XIV we have found on falling transition curves seven cases of abnormal compressibility, and only two of normal. (By "abnormal" compressibility we mean that the phase of larger volume is less compressible). The model of Figures 34 and 35 also suggests the reason for this. In general, two effects contribute to the apparent compressibility of a substance; the actual change of volume of the molecules under pressure, and the closing up of the free spaces which provide some of the possibility of temperature agitation. Now evidently in Figure 34 there can be very little free space for temperature agitation, because if the centers of the molecules are separated by only a slight distance from the position of tight packing a very small angular displacement suffices to carry the corners out of register with each other, and the structure becomes unstable. In the structure of Figure 35, however, much greater separation of the centers from the position of actual contact is possible before a given angular displacement carries the corners past each other. The phase of smaller volume is more compressible, therefore, because in it there is more free space from which the temperature agitation may be excluded. One does not care to speculate much about the behavior of the specific heats, now that the theorem of equipartition is known not to be valid, but it would seem in general as if the phase of smaller volume would have the most freedom, and so the greater specific heat, although it is conceivable that if the energy of temperature agitation were chiefly energy of the nucleus, that the nucleus might have less freedom at the smaller volume, and so the specific heat of the phase of smaller volume be less.

All the preceding considerations apply to transitions of the ice type. The ordinary type of transition, in which the form stable at the higher temperature has the larger volume, may be thought of as one in which projections on one molecule fit into depressions on others, the centers

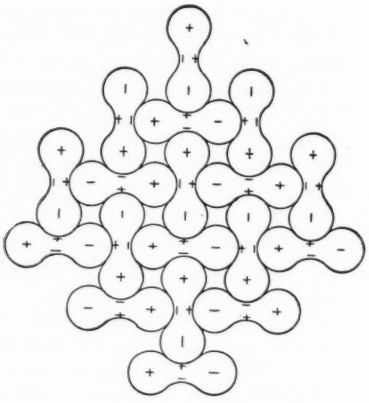

FIGURE 36. Hypothetical substance. This arrangement does not allow temperature agitation of much violence.

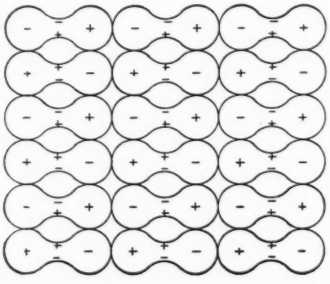

FIGURE 37. The atoms of Figure 36 in another arrangement occupying more volume and allowing greater violence of agitation.

of force being on the projections or in the depressions. The projections or depressions are such that the molecules must be fitted together rather precisely to secure proper alignment. Temperature throws

them out of these nicely fitted positions into other positions further apart, of less mean internal pressure, and greater freedom for temperature agitation. Figures 36 and 37 show a possible scheme for the low and high temperature modifications. The effect of increased pressure is obviously to compact the phase of smaller volume, so that increased temperature is needed to pull the molecules apart. As a general rule, we would expect the phase of smaller volume to be more incompressible, but if the molecule is unequally compressible in different directions, as it must be, it is evident that under the proper conditions the phase of larger volume may be more incompressible.

The models of Figures 36 and 37 are suggestive in several other particulars. It may be mentioned in the first place that these units may be built up into several other structures, two at least of which have a still smaller volume than that of Figure 36, thus showing the possibility of a number of polymorphic forms. The arrangement of Figure 36 is evidently one which will show considerable persistence; it will stand a good deal of superheating and the transition velocity will be low, whereas that of Figure 37 will stand relatively slight superheating (or subcooling) and the transition velocity will be high. Figure 36 also illustrates a point made in a previous paper,[43] namely that if an atom passes from one modification to another it must rise from its position of equilibrium and pass through an intermediate position of greater potential energy. It is evident that some initial work will be required to pull an atom from the position of Figure 36, even if this work is more than returned when it settles down into the final position of equilibrium. In this way the band of indifference may be accounted for. It is also evident that if the two phases of Figures 36 and 37 are in contact there will be a field of force over the surface of each phase in which the atoms will tend to orient themselves in the appropriate positions. The tendency to pass from one phase to another is not an affair of absolute instability of one phase, but is a relative instability shown only in the presence of the other phase; this point was also mentioned in the paper just cited.

One implication of the view that regards crystals as built up from blocks of definite shape is to be especially insisted on. Only in exceptional cases will the edifice constructed from the blocks be such that there are no unfilled crevices around the corners, and in no case where there are two possible structures of different volumes will such empty spaces be absent in at least one of the structures. These empty

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43 I. p. 86.

spaces are to be thought of as playing an essential part in the phenomena of polymorphism. In the face of such changes as that from ice I to III with a change of volume of 17% and NH_4Cl, I to II, with a change of volume of 15%, it is most difficult to resist the conviction that there are empty spaces of relatively large size and that they are essentially concerned in polymorphic changes. Facts like these I find it most difficult to reconcile with Professor T. W. Richards' point of view that in a solid or a liquid nearly all the available space is completely filled by the atoms, and that the changes of volume produced by pressure or changes of temperature are the result of changes of volume of the atoms themselves. That the atoms are compressible, and that the compressibility enters essentially into many phenomena there can be no question, but it seems to me just as unquestionable that there must be vacant spaces around the corners which also play an important part in many phenomena, including preëminently the phenomena of polymorphism. The difficulty of Professor Richards' view seems to me increased by the fact that in many cases the phase of smaller volume is the more compressible.

These suggestions are no more than very rough indications of what may be the nature of the effects. The actual molecules are three dimensional instead of two; this alone will cause profound differences in the way in which a uniformly filled space can be built up from uniform elements. Furthermore, the elements in the diagrams have been chosen so simply that the crystalline framework of both polymorphs is the same, whereas only in isolated cases is this true in nature. It is of interest, however, that we have here a suggestion as to why it is that different phases may belong to the same system. We have also considered only one kind of element, whereas the majority of crystals are built up from different kinds of atoms. This alone will allow possibilities of enormously greater complications. The actual shape of the molecules are probably much more complicated and not so exaggerated as those shown above, and there must be a greater multiplicity of arrangements in which they can be piled. But the diagrams do illustrate the fertility of the fundamental idea; that by ascribing to the molecules definite shapes as well as localized centers of force, systems may be built up which show many of the complications of actual polymorphic forms.

The bewildering complexity shown by various polymorphic transition throws light on a group of phenomena of another kind. In a previous paper (G), I have described the effect of high pressure on the thermodynamic properties of a number of liquids. It appeared that

under the more moderate pressures all the liquids tend to a more or less common type of behavior, but that at higher pressures the most varied abnormalities make their appearance, each liquid behaving in its own characteristic way. These abnormalities are doubtless to be explained by the increasing approach to some sort of order brought about when the molecules are squeezed closer together by high pressure. As pressure and temperature shift the predominating type of order in the relation of the molecules may change also, and we get the varied effects which we know occur when the arrangement of the atoms is altered as it is in a polymorphic transition. It seems most natural to suppose that the same sort of considerations and the same mechanism that will some day be discovered to account for polymorphic changes will also account for the complicated phenomena in liquids at high pressures.

Summary.

New data are presented for the polymorphic transitions of a number of substances between 0° and 200° and to 12000 kgm. All of the substances which I have examined which have shown no polymorphic changes in this same range are enumerated. This enumeration includes also all the substances with polymorphic forms, and classifies them according to chemical structure. The total number of substances examined to date is nearly 150. The discussion deals with all the phase diagrams examined in this series of papers. There is no simple type toward which all polymorphic diagrams tend at high pressures, nor are there a few common types. The complication is very great; probably solid transitions of any type whatever exist, except those involving a critical point. It is suggested that in order to explain these complicated phenomena the effect of the shape of the atoms is the next factor to be considered, and it is shown in detail by considering several artificial examples that assemblages of units of definite shape provided with localized centers of force are capable of exhibiting the variety of behavior which actual polymorphic substances show.

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